Fluoro-Substituted Metal Phthalocyanines for Active Layers of Chemical Sensors

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A long time ago, metal phthalocyanines bearing electron-withdrawing fluorine substituents were synthesized, but interest in the study of their films has emerged in recent decades. This is due to the fact that, unlike unsubstituted phthalocyanines, films of some fluorinated phthalocyanines exhibit the properties of n-type semiconductors, which makes them promising candidates for application in ambipolar transistors. Apart from this, it was shown that the introduction of fluorine substituents led to an increase in the sensitivity of phthalocyanine films to reducing gases. This review analyzes the state of research over the last fifteen years in the field of applications of fluoro-substituted metal phthalocyanines as active layers of gas sensors, with a primary focus on chemiresistive ones. The active layers on the basis of phthalocyanines with fluorine and fluorine-containing substituents of optical and quartz crystal microbalance sensors are also considered. Attention is paid to the analysis of the effect of molecular structure (central metal, number and type of fluorine substituent etc.) on sensor properties of fluorinated phthalocyanine films.

Keywords: metal phthalocyanines; fluoro-substituents; chemiresistive sensors; optical sensors; quartz crystal microbalance; thin films

1. Introduction

Metal phthalocyanines (MPc) belong to the class of coordination compounds with organic ligands. The phthalocyanine molecule consists of four isoindole fragments connected through nitrogen atoms of the tetrabenzo-porphyrine macrocycle. Since their discovery, phthalocyanines have been widely used not only as dyes and catalysts [1–3], but also in advanced technological fields, for example, as active layers of solar cells [4,5], diodes [6,7], and transistors [8,9]. Due to their ability to change conductivity during adsorption of various gases, the application of metal phthalocyanines as sensing layers of chemiresistive sensors is of particular interest [10–12]. On the one hand, phthalocyanine macrocycles can chelate with almost all metals of the periodic table. On the other hand, various types of substituents can be introduced into their macroring [13–16]. Due to such versatility in their structure, they exhibit different sensitivity to a number of analytes.

Another important property of metal phthalocyanines, which makes them useful for the modification of electrodes of electrochemical sensors, is their electrocatalytic and electron mediator capability [23–26]. Electrodes modified with metal phthalocyanines or their composite materials were shown to be used in amperometric, potentiometric and biosensors as well as voltammetric electronic tongues for the detection of various analytes.

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among them dopamine, glucose, cysteine and so on [27,28]. Among the wide variety of phthalocyanines, fluorinated derivatives occupy a special place due to the influence of fluoro-substituents on the redox potential of compounds and intermolecular interaction with analytes.

Fluorinated porphyrinoids have been the subject of several reviews over the past few years. The synthesis of fluorinated porphyrinoids and some aspects of their application for the creation of new photonic materials have been the subject of several reviews [17,29,30]. In a book chapter written by P. Stuzhin [17], an overview of different methods of synthesis of phthalocyanines, subphthalocyanines and porphyrazines bearing fluorine atoms and/or perfluorinated alkyl or aryl groups was provided. S. Casa and M. Henary published another critical review [30], which covers the aspects of synthesis and the application of selected fluorne-containing fluorophores. Among other fluorine-containing molecules, the authors analyzed the methods of synthesis of metal phthalocyanines bearing fluoroalkyl and fluoroaryl moieties and their application as photosensitizers for photodynamic therapy. The mini review written by Gorun et al. [31] summarizes recent researches of fluoroalkyl-substituted metal phthalocyanines, in which the majority of C–H bonds are replaced by a combination of fluoro- and perfluoroalkyl groups as bioinspired catalytic materials. A review article written by Dinesh K. Bhupathiraju et al. [29] was focused on the reactions of nucleophilic substitution of fluorinated analogues of porphyrins, phthalocyanines, chlorin, phenylcorrole and bacteriochlorin. The authors also considered their electrocatalytic and light-absorbing properties important for various biomedical applications as well as sensing behavior. However most of the presented data in this field of chemical sensors were devoted to the use of porphyrin derivatives as fluorescence sensors for the detection of dissolved oxygen, and only very limited examples of the application of fluoro-substituted phthalocyanines in other types of sensors were given. Apart from this, questions concerning the effect of the number and type of fluorine or fluorne-containing substituents on the sensor performance were not sufficiently answered.

This review analyzes the state of research over the last fifteen years in the field of applications of fluoro-substituted metal phthalocyanines as active layers of gas sensors, with a primary focus on the sensors with electrical response (Scheme 1). Attention will be paid to the analysis of the effect of molecular structure (central metal, number and type of fluorine substituent etc.) on sensor properties of the films of fluorinated phthalocyanines.

![Scheme 1](image)

**Scheme 1.** Schematic representation of the application of fluoro-substituted metal phthalocyanines as active layers of gas sensors.
2. Brief Overview of Fluorinated Phthalocyanines and Preparation of Their Thin Films

A large variety of phthalocyanines with fluorine and/or fluorine-containing substituents has been synthesized and investigated [32–35]. In this section, we consider only those fluoro-substituted phthalocyanines, which were used for the preparation of active layers of chemical sensors in the publications analyzed in this review. The literature analysis shows that both phthalocyanines with fluorine atoms directly in the aromatic rings and phthalocyanines bearing fluoroalkyl and fluoroaryl substituents are widely used for the preparation of active layers of gas sensors. Some example of such fluorinated MPc derivatives are summarized in Table 1. The methods of their synthesis have already been discussed in detail in recent reviews [17,30].

Table 1. Structures of fluoro-substituted phthalocyanines.
For the use of phthalocyanines as active layers of chemical sensors, it is important that a phthalocyanine is deposited as a thin film with a controlled structure and morphology on the surface of an electrode. The method of deposition of films is determined by the properties of the compound itself. It is known that phthalocyanines with F-substituents directly in the aromatic rings (Compounds 1–3, Table 1) are insoluble in...
common organic solvents, but can be sublimed in vacuum with the formation of smooth and homogeneous films [21,32,36].

Thin films of MPcF_{x} (x = 4, 8, 16) deposited by physical vapor deposition (PVD) or organic molecular beam deposition techniques are usually polycrystalline and have preferable orientation of polycrystallites relative to the substrate surface (Figure 1a–c) [37]. Their orientation degree and size of crystallites are dependent on the substrate material and deposition conditions [22,38,39], that is, the rate of film growth and substrate temperature [40]. In turn, the structure and surface morphology of fluorinated phthalocyanine films have a significant effect on their conductivity, charge carrier mobility, and sensor performance [41–43]. Summarizing the data on the deposition of films of fluorinated metal phthalocyanines given in the literature, the main conditions of these processes can be identified. The films are deposited in ultra-high (~10^{-10} Torr) or high vacuum (~10^{-5}–10^{-6} Torr) at evaporator temperatures from 300 to 480 °C [38].

![Topographic AFM images](image_url)

**Figure 1.** Topographic AFM images (2 μm × 2 μm) of CoPcF_{16} thin films grown at different elevated substrate temperatures: 100 °C (a), 220 °C (b), and 290 °C (c). Adapted from [37] with permission from Elsevier. XRD patterns of CoPcF_{x} (x = 0, 4, 16) thin films (d).

Similarly to the films of unsubstituted metal phthalocyanines, XRD patterns of MPcF_{x} films usually contain a single strong diffraction peak in the range from 5° to 7° 2θ, which is a typical feature of thin films with a strong preferred orientation (Figure 1d).

It was shown that in contrast to MPc (M = Cu, Co, Zn), which are able to form α- and β-modifications [44,45], CuPcF_{4}, CoPcF_{4}, and ZnPcF_{4} crystallize only in one triclinic (P-1 space group) phase [32,46]. At the same time, two polymorphs α-CuPcF_{16} (P-1 space group, Z = 1) [47], forming on a substrate at room temperature, and triclinic β-CuPcF_{16} (P-1 space group, Z = 2) growing on a substrate heated to 360 °C [48], were identified in the case of CuPcF_{16}. Thin films of fluorinated metal phthalocyanines with non-planar structure (e.g., PbPcF_{4}, VOPcF_{4}, etc.) were also investigated. PbPc films were shown to consist of two crystal phases, triclinic and monoclinic, while PbPcF_{4} and PbPcF_{16} films are single-phase, having the same structures as their single crystals, in tetragonal (I4) and...
triclinic (P-1) space groups, respectively [49]. VOPc and VOPcF₄ crystallites have strong preferred orientation relative to the substrate surface [50].

The introduction of fluoroalkyl or fluoroaryl substituents (Compounds 4–16, Table 1) leads to the better solubility of phthalocyanine derivatives in organic solvents [51–53]. For this reason, the drop cast, spin coating and jet spray techniques are used for the preparation of their films on different substrates and electrodes [33,54]. Duan et al. [52] utilized a phase-transfer method for the preparation of the layers of (trifluoromethyl)phenoxy-substituted phthalocyanine derivatives (Compounds 6, Table 1), while Dong and co-authors [55] deposited films of metal-free phthalocyanines bearing trifluoroethoxy-substituents by a solution-based quasi-Langmuir-Shäfer (QLS) method. The structure and morphology of the films were dependent on the phthalocyanines’ molecular structure and the deposition technique. For example, the drop-casted films of ZnPc(OCH₂(CF₂)₆CF₃)₈ [56] and H₂Pc(OCH₂(CF₂)₆CF₃)₄ [57] were less crystalline than vacuum-deposited films, and they had a tendency to form J-type molecular stacking structures. The use of a phase-transfer method led to the formation of crystalline films of M[Pc(OCH₂C₃F₇)₈] (M = 2H, Zn) [58] and MPc [α-O(4-CF₃-Ph)]₄ (M = 2H, Co) [52] with a helical ribbon-like structure with a ribbon width of about 1.5–5 μm and length over 30 μm. Thus, when producing layers for chemical sensors, the film-deposition parameters must be strictly controlled, in order to obtain films of a certain phase composition and ordering.

3. Active Layers of the Devices with Electrical Sensor Response

To date, metal phthalocyanines with various substituents are widely investigated and utilized as active layers of chemical sensors with electrical response for the detection of different gases due to their semiconductor behavior and ability to change their resistance upon interaction with various gases [59–61]. Among them, fluorinated phthalocyanines are known to use, as active layers of chemical sensors toward ammonia [21,62], chlorine [63,64], nitrogen dioxide [52,65] and hydrogen [50,66]. The sensor devices are mostly based on chemiresistors [21,67,68] and organic field effect transistors (OFET) [69]. For the preparation of the standard chemiresistive sensors, films are deposited onto the substrates with interdigitated electrodes. In the case of OFET, there is a broad range of various configuration designs, as summarized in a recent review article on gas sensors based on OFET structures (Figure 2) [70].

It is known that the introduction of electron-withdrawing substituents, such as fluorine, can change the charge transport properties of metal phthalocyanines from p-type to n-type. For instance, MPc (M = Cu, Co, Zn) are typical p-type materials, while the corresponding MPcF₁₆ derivatives demonstrate n-type semiconductor behavior [71]. MPcF₄ (M = Cu, Co, Zn) are known to exhibit both p-type and n-type behavior, depending on central metals and environment [72]. For this reason, fluorinated metal phthalocyanines are widely used as an active layer in both unipolar and ambipolar transistors combining bilayer structures or blends of n- and p-type MPCs [9,20,73].

Bouvet et al. [74] suggested one more principle of transduction based on molecular semiconductor-doped insulator (MSDI) heterojunction (Figure 3).
In short, the principle of operation is in the tuning effect exerted by the doped insulator layer at the level of the heterojunction in the electronic properties of the LuPc2 semiconductor, which demonstrates inverted sensor response to accepting and donating analyte molecules. This idea was described in more detail in their recent review [75]. In such molecular semiconductor-doped insulator heterojunction structures the top layer (e.g., LuPc2) has a very high carrier concentration, while such relatively poor semiconductors as fluorinated metal phthalocyanines are used as sublayers. Electrons and holes at definite conditions may be injected in the sublayer, which justify their name as molecular semiconductor-doped insulators [75].

The main characteristics of sensors with electrical sensor response with fluorinated metal phthalocyanines as active layers are summarized in Table 2.
| Active Layer | Sensor Type | Analyte | Investigated Range, Ppm | LOD, Ppm | Recovery Time, S | Ref. |
|--------------|-------------|---------|------------------------|---------|-----------------|-----|
| ZnPcF<sub>16</sub> | Chemiresistive | NH<sub>3</sub> in N<sub>2</sub>, H<sub>2</sub> in N<sub>2</sub> | 0–1000 0–2000 | n/a | Several hours | [76] |
| ZnPcF<sub>16</sub> | Chemiresistive | NH<sub>3</sub>, N(CH<sub>3</sub>)<sub>3</sub>, NH<sub>2</sub>CH<sub>3</sub>, N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> | 0.72 (NH<sub>3</sub>) | n/a | n/a | [77] |
| CoPc<sub>2</sub> | Chemiresistive | NH<sub>3</sub> | 10–50 | 2.5 | 30 (20 ppm) | [62] |
| PdPcF<sub>16</sub> | Chemiresistive | NH<sub>3</sub>, H<sub>2</sub> | 10–50 1000–5000 | n/a | 50 500 | [68] |
| MPc<sub>x</sub> (M = Cu, Co, Zn, x = 4, 16) | Chemiresistive | NH<sub>3</sub> | 0.1–50 | 0.1 (for ZnPcF<sub>4</sub>) | n/a | [21] |
| PbPcF<sub>4</sub> | Chemiresistive | NH<sub>3</sub> | 1–5 | n/a | 90–220 | [49] |
| VOPcF<sub>4</sub> | Chemiresistive | NH<sub>3</sub>, H<sub>2</sub> | 10–50 10–500 | n/a | 230 (30 ppm) 50 (300 ppm) | [50] |
| CuPcF<sub>16</sub>/pNIDPP, CuPcF<sub>16</sub>/pNIDMP | MSDI | NH<sub>3</sub> | 1–50 | -1 0.228 | n/a | [78] |
| CuPcF<sub>16</sub>/LuPc<sub>2</sub> on bare ITO, CuPcF<sub>16</sub>/LuPc<sub>2</sub> on DMBz/ITO | MSDI | NH<sub>3</sub> | 30–90 | n/a | n/a | [79] |
| CuPcF<sub>16</sub>/LuPc<sub>2</sub> | MSDI | NH<sub>3</sub> | 1–90 | 0.28 (RH 50%) 0.14 (RH 50%) | n/a | [80] |
| CoPc[β-O(4-CF<sub>3</sub>-Ph)<sub>4</sub>]H<sub>2</sub> | Chemiresistive | NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S | Dependent on the analyte | 0.003 0.03 0.198 0.25 (to NO<sub>2</sub>) | n/a | [52] |
| H<sub>2</sub>Pc(OCH<sub>2</sub>CF<sub>3</sub>)<sub>4</sub> (Compounds 6, Table 1) | Chemiresistive | NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S | Dependent on the analyte | 0.003 0.03 0.198 0.25 (to NO<sub>2</sub>) | n/a | [52] |
| H<sub>2</sub>Pc(OCH<sub>2</sub>CF<sub>3</sub>)<sub>4</sub> (Compounds 6, Table 1) | Chemiresistive | NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S | Dependent on the analyte | 0.003 0.03 0.198 0.25 (to NO<sub>2</sub>) | n/a | [52] |
| CoPc<sub>5</sub> (Compound 12, Table 1) | Chemiresistive | NH<sub>3</sub> | 0.3–50 | 0.3 | 40 (5 ppm) | [51] |
| Gd<sub>2</sub>[Pt(OHPhF)<sub>3</sub>]Tb[Pt(OHPhF)<sub>3</sub>] (Compounds 11, Table 1) | Chemiresistive | NH<sub>3</sub> | 1–20 | - 0.151 126 103 (20 ppm) | [82] |
| CuPcF<sub>16</sub>/rGO | Chemiresistive | Cl<sub>2</sub> | 0.06–3 1.41·10<sup>-3</sup> | 551 | | [83] |
| CuPcF<sub>16</sub>/SWCNT | Chemiresistive | Cl<sub>2</sub> | 0.04–2 0.05·10<sup>-3</sup> | 150 (500 ppb) | [84] |
| CuPcF<sub>16</sub>/SWCNT | Chemiresistive | Cl<sub>2</sub> | 0.1–2 0.27·10<sup>-3</sup> 0.85·10<sup>-3</sup> | n/a | [63] |
| MPCF<sub>16</sub>/SWCNT (M = Co, Zn, Cu) | Chemiresistive | Cl<sub>2</sub> | 0.04–2 0.04·10<sup>-3</sup> | n/a | [85] |
| ZnPcF<sub>16</sub>/MWCNT | Chemiresistive | Cl<sub>2</sub> | 0.01–2 0.06·10<sup>-3</sup> | n/a | [64] |
| Compound 7 (Table 1)/SWCNT | Chemiresistive | NH<sub>3</sub> | 1–50 | 0.78 | 170 (10 ppm) | [86] |
3.1. Sensors Based on MPcF_x Films Obtained by PVD

The literature analysis shows that the films of MPcF_x (x = 4, 8, 16) with M = Cu, Co, Pd, Zn, VO are most widely used as active layers of sensors for ammonia detection. It was shown that fluorine substituents decrease the electron density of the aromatic ring and increase the oxidation potential of the MPc molecule [87]. As a result, fluorosubstituted phthalocyanines exhibit a higher sensor response to reducing gases [88] such as ammonia. Schollhorn et al. [76] were the first to show that hexadecafluoro-substituted zinc phthalocyanine ZnPcF_{16} films prepared by vacuum evaporation exhibited a higher sensitivity to gaseous ammonia and hydrogen than their unsubstituted analogues. Their conductivity was measured during exposure to the reducing gases NH_3 and H_2 diluted in N_2. Later, Xingfa Ma and coworkers [77] compared the sensitivity of ZnPc and ZnPcF_{16} films to ammonia, trimethylamine and methylamine and found that fluorination led to a significant improvement in sensitivity. ZnPcF_{16} films were shown to have good selectivity and stability and to recover completely after purging with high-purity N_2 at room temperature.

More systematic studies of the sensor response of MPcF_x (M = Cu, Co, Zn, Pd, VO, Pb; x = 4, 16) films toward gaseous NH_3 were carried out by our research group using a chemiresistive method. The sensor response of MPcF_x was compared with that of unsubstituted MPc films to reveal the effects of F-substituents and central metals on the sensing performance (Table 2) [21,49,50,62,68]. The effect of F-substituents on the sensor response to NH_3 was studied using films of zinc, copper and cobalt phthalocyanine derivatives MPcFx (x = 0, 4, 16) as examples [21] (Figure 4). It is important to mention that the introduction of gaseous NH_3 to the gas chamber leads to an increase in the resistance of MPcF_4 films (Figure 4a). This behavior was typical for p-type organic semiconductors and was also observed for the films of unsubstituted metal phthalocyanines [89]. In contrast to MPc and MPcF_x, MPcF_{16} films demonstrate a decrease in their resistance upon interaction with electron donor NH_3 molecules (Figure 4b). It is known that MPcF_{16} films demonstrate n-type semiconducting behavior due to the effect of electron-withdrawing F-substituents [90].

According to the mechanism of semiconductor sensors described in the literature [91,92], the formation of charge-transfer complexes by coordination of O_2 to MPc occurs at the air/MPc interface and at grain boundaries, which leads to the formation of oxidized MPc^+ and O^{2-} species [93,94]. When a p-type semiconductor gas sensor is exposed to the reducing gases (e.g., NH_3), the electrons injected into the material through the oxidation reaction between the reducing gas and the O^{2-} species on the semiconductor surface decrease the concentration of holes in the layer, which in turn increases the resistance of MPc film [95]. A schematic diagram of the sensing mechanisms of MPc sensors is shown in Figure 3. When an n-type semiconductor is exposed to a reducing gas, ionized oxygen anions are used to oxidize the reducing gas, and the released electrons inject into the semiconducting core, which decreases the sensor resistance proportionally to the concentration of reducing gas-analyte [92]. In the case of oxidizing gases (e.g., NO_2, Cl_2) a surface adsorption mechanism is also used. In contrast to reducing gases, the
doping of n-type semiconductor by NO₂ leads to the capture of carriers, thereby reducing their current [55].

Although observations of changes in the measured current of MPc sensing layers exposed to NH₃ and other analytes are explained by electron transfer, the interaction sites in the porphycene macrocycle or metal center are still a matter of discussion. According to the data of most works, the most energetically favorable site of NH₃ and NO₂ molecule binding is the central metal of MPc molecules [96–99]. These conclusions were based only on the quantum chemical calculations. At the same time, the experimental investigations of the interaction sites are sporadic [10,100]. For example, Saini et al. [100] used Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) for investigation of interaction of CuPcR₄ (R=–OC₄H₄) with chlorine. They found a shift of the bands at 253 and 1529 cm⁻¹, which were attributed to the Cu–Nₐ stretching vibration and the vibration associated with the cavity change in the porphycene macrocycle, respectively, after interaction with Cl₂. That was in good correlation with the shift of Cu 2p peaks in XPS spectrum of the exposed films. Thus, the studies revealed that central metal ions of CuPcR₄ molecules were the predominant sites of Cl₂ adsorption. Chia et al. [10] used in situ X-ray absorption spectroscopy (XAS) to investigate the interaction of CuPc with NH₃ and NO₂ molecules. In contrast to the previous case, the first derivative of XANES suggested low or a lack of axial position coordination on the Cu metal center. On the other hand, the interaction on the macrocycle was supported by the EXAFS. From the EXAFS of CuPc with NO₂, the interaction was suggested to be at the pyrrole moiety of the Pc macrocycle, while in the case of NH₃ on the benzo moiety or bridging atom. The experimental investigations of the interaction sites in the case of fluorinated MPcs were not carried out.

It was also shown that the sensor response decreased in the order of MPcF₄ > MPcF₁₆ > MPc (Figure 4). MPcF₄ films showed the highest sensor response to ammonia among the investigated porphycene derivatives; their response was 3–10 times higher than that of MPcF₁₆ films, and 30–70 times higher than that of MPc films. All films exhibited a reversible sensor response at room temperature, with the response time of 10–25 s and recovery time no more than 2 min [21].

The sensor response toward ammonia changed also in the same order for lead phthalocyanine derivatives PbPcF₄ > PbPcF₁₆ > PbPc, and the sensors demonstrated completely reversible sensor response at room temperature [49]. The effect of central metals on the sensor response of MPcF₄ and MPcF₁₆ to NH₃ was also investigated by our group. Figure 5 summarizes the data on the dependence of the sensor response of MPcF₄ and MPcF₁₆ (M = Cu, Co, Zn, Pb, VO) on NH₃ concentration.

![Figure 5](image)

**Figure 5.** Dependence of the sensor response of MPcFₙ (M = Co, VO, Zn, Pb, Cu, x = 4 (a), 16 (b)) films on ammonia concentration.

Both in the case of tetrafluorinated and perfluorinated derivatives, the sensor response decreased in the order Co > VO–Zn > Pb > Cu. The data for phthalocyanines of Co, Zn and Cu were in reasonably good correlation with the results of quantum chemical calculations of the binding energy between NH₃ and phthalocyanine molecules as well as changes in the values of effective charge on NH₃ molecule.
More detailed study of the performance of ZnPcF₄-based sensor were performed by Klyamer et al. [21]. ZnPcF₄ films were shown to exhibit the detection limit of ammonia 0.1 ppm, and can be used for its selective detection in the presence of some reducing gases and volatile organic compounds, namely acetone, dichloromethane, carbon dioxide and ethanol (Figure 6). Moreover, the ZnPcF₄ films can be used for the detection of NH₃ in the gas mixture simulating exhaled air (N₂ 76%, O₂ 16%, H₂O 5%, and CO₂ 3%) and at relative air humidity up to 70%.

![Figure 6](image_url)

**Figure 6.** (a) Response of a ZnPcF₄ film to ammonia (10 ppm), acetone (1000 ppm), dichloromethane (104 ppm), carbon dioxide (104 ppm), ethanol (104 ppm). (b) Sensor response of a ZnPcF₄ layer toward ammonia in the concentration range from 1 to 4 ppm, in air (1) and in a mixture of gases with the composition close to exhaled air of healthy people (N₂ 76%; O₂ 16%; H₂O 5%; and CO₂ 3%) (2) [21].

Apart from the sensors to ammonia, MPcF₃ films are utilized as active layers of chemiresistive sensors for the detection of hydrogen. For example, Parkhomenko et al. [68] compared the sensor response of PdPcF₁₆ films to hydrogen (1000–5000 ppm) with that of PdPc films. It was found that the sensitivity of PdPc film to hydrogen was slightly higher than that of the PdPcF₁₆ film. VOPcF₄ were shown to be also sensitive to hydrogen [50], but, similarly to palladium derivatives, the sensor response of VOPcF₄ film was slightly less than in the case of unsubstituted vanadyl phthalocyanines films.

Fluorinated MPc-based organic filed effect transistors (OFET) or organic thin film transistors (OTFT) with p–n heterojunction were also investigated for detecting various gases and volatile organic compounds (Table 2). For example, Yang et al. [69] prepared OFET structures with CuPcF₁₆ as an n-type semiconductor and SiO₂ as a dielectric, and tested them as active layers of sensors for the detection of dimethyl methylphosphonate (DMMP) and methanol in comparison with similar OFETs on the basis of p-type CuPc layers. Other analytes, namely diisopropyl methylphosphonate (DIMP), H₂O and nitrobenzene, were also determined to check the sensor selectivity. It was shown that the responses were of opposite sign for n-type and p-type OFETs for all five analytes. The authors observed a difference in sensitivity to DMMP (68 ppm) and MeOH (1520 ppm): at the same concentration, the n-channel OFET (CuPcF₁₆) had the larger response to DMMP than the p-channel analogue (CuPc), while the p-channel OFET had the larger response to MeOH than the n-channel transistor (Figure 7).

Modulation of interfacial charge alignments by molecular engineering in organic heterojunction devices is a promising strategy to improve their conductivity and sensor sensitivity. Sensing properties of the heterojunction devices based on fluorinated metal phthalocyanines are widely investigated. Wang [81] and Zhang [65], with their co-authors, reported the results of investigations of an OTFT sensor with p–n heterojunction in MPCF₁₆/MPc thin films. A sensor device based on a ultra-thin TiOpc film as a bottom layer and a CuPcF₁₆ film as a top layer demonstrated an increased relative sensor response to nitrogen dioxide below 5 ppm with a detection limit of up to 250 ppb at room temperature (Figure 8) [81].
DMMP in air and N2 at 25 °C. (to MeOH than the n-channel transistor (Figure 7). than the p-channel analogue (CuPc), while the p-channel OFET had the larger response. responses were of opposite sign for n-type and p-type OFETs for all five analytes. The au-
slightly less than in the case of unsubstituted vanadyl phthalocyanines films.
phthalocyanines are widely investigated. Wang [81] and Zhang [65], with their OFET structures with CuPc as an n-type semiconductor and SiO2 as a dielectric, and tested them as active layers of sensors for the detection of dimethyl methylphosphonate (DMMP) and methanol in comparison with similar OFETs on the basis of p-type CuPc layers. Other analytes, namely diisopropyl methylphosphonate (DIMP), H2O and nitro-
Figure 7. (a) Chemical responses of n-channel CuPcF16 (a) and p-channel CuPc (b) ChemFETs to DMMP in air and N2 at 25 °C. (c) The sensitivities of n- and p-channel ChemFETs to nerve agent simulants (DMMP and DIMP) and other analytes: MeOH, H2O, and NB at 25 °C. The sensitivity is in logarithmic scale. Reprinted from [69] with permission from AIP Publishing.

Figure 8. (a) Relative response of the three devices to NO2 pulse as a function of time. The relative response is defined as normalized increase in device current. (b) The section view of bilayer device structure and the molecular structure of CuPcF16 and TiOPc. Reprinted from [82] with permission from Elsevier.

Similar heterojunction organic thin film transistors based n-type CuPcF16 and p-type CuPc were also utilized to detect NO2 [65]. The authors investigated the effect of CuPc film thickness in the range from 5 to 20 nm on the devices’ performance. It was found that the sensor with a CuPc film with a thickness of 15 nm had optimal sensing characteristics.

Bouvet and co-authors in the series of works [74,79,80] demonstrated that conductometric gas sensing devices based on organic heterojunction between poor conducting and high conducting organic semiconductors had high sensitivity and selectivity toward redox gases (Table 2). The sensing devices benefited from the organic heterojunction effects, in which opposite charges (e− and h+) were accumulated at the interface of a bilayer film because of the work function difference between the semiconducting layers, enhancing the charge carriers mobility along the interface. For this purpose, they used a combination
of a CuPcF \(_x\) (\(x = 8\) or 16) film as a poor conducting layer and LuPc\(_2\) as a high conducting layer in a bilayer heterojunction configuration [74,79,80] (Figure 9). It was found that the n-MSDI on the basis of LuPc\(_2\) and CuPcF\(_{16}\) thin films exhibited a response to NH\(_3\) opposite to that of a LuPc\(_2\) resistor, and the relative response was ca. seven times higher [74]. Apart from this, it was less sensitive to the presence of humidity in air. The same group of authors in their other work demonstrated that the modification of ITO substrate via electrografting of 1,4-dimethoxybenzene led to an increase in the n-MSDI sensitivity from 1.5 to 3\% ppm\(^{-1}\) in the range of 1–9 ppm, compared to n-MSDI without surface modification (Table 2) [80]. This effect appeared to be due to the change in interfacial energy barrier resulted from the modification of the electrode work function, because of the formation of interface dipoles [101].

Figure 9. Architecture of the MSDI devices: (a) showing the molecular structure of the phthalocyanine materials; and (b) a schematic view of the organic-based device. Reprinted from [74] with permission from Royal Society of Chemistry.

The sensor performance of MSDI heterostructures based on LuPc\(_2\) and CuPcF\(_{16}\) towards 35 ppm of NH\(_3\) in an Ar atmosphere were also compared with that of CuPcF\(_x\) (\(x = 0, 8, 16\)) films [74].

It was found that LuPc\(_2\)/CuPcF\(_8\) heterostructures had lower sensitivity to NH\(_3\) than LuPc\(_2\)/CuPc ones, while LuPc\(_2\)/CuPcF\(_{16}\) heterostructures exhibited a completely reversed response, and their sensitivity to ammonia drastically increased. Interestingly, CuPc/LuPc\(_2\) MSDIs showed an increase in current when exposed to ozone (90 ppb) and a decrease in current when exposed to NH\(_3\) (35 ppm), indicating the p-type nature of the device. In contrast, the CuPcF\(_{16}\)/LuPc\(_2\) MSDIs revealed the opposite trend manifested in the n-type nature of the device [74,102].

In their other work [78], Bouvet et al. fabricated organic heterojunction devices by sequential deposition of CuPcF\(_{16}\) on a glass substrate lithographically patterned with indium tin oxide (ITO) interdigitated electrodes (IDEs) and two different types of porphyrin tapes (pNiDPP and pNiDMP originated from Ni(II) 5,15-(diphenyl)porphyrin (NiDPP) and Ni(II) 5,15-(dimesityl)porphyrin (NiDMP) monomers, respectively). The investigated devices revealed high response toward ammonia, fast sorption kinetics, stable baseline, and low interference from relative humidity fluctuations. The device based on a CuPcF\(_{16}\)/pNiDMP bilayer structure exhibited sensitivity about 0.4\% ppm\(^{-1}\) and LOD up to 228 ppb.

A summary of the data on the study of sensors based on MPcFx films obtained by the PVD method shows that these films are mainly used for the detection of ammonia. It was shown that they exhibited a quite low detection limit, reaching 0.1 ppm, and quick response and recovery times. Apart from this, the detection of ammonia can be performed in the presence of carbon dioxide and volatile organic vapors as well as in a humid atmosphere. This makes MPcFx films promising candidates for the determination of low concentrations (below 2 ppm) of ammonia as a biomarker of renal diseases [103,104] in exhaled air. The analysis of the literature has shown that, currently, the work on the practical application
of phthalocyanine films for the determination of biomarker gases is in its infancy, so the development of research in this direction is of great interest for creating a new direction of medical diagnostics.

On the other hand, the bottleneck for using MPcFx sensors to detect ammonia or other analytes in complex gas mixtures, including amines and oxidizing gases such as Cl₂, SO₂, and NOₓ, is their low selectivity. To overcome this obstacle, it is common practice to create sensor arrays that include sensor layers, which have different sensitivity to the analyzed components of the gas mixture. Currently, no systematic studies of phthalocyanine-based sensor arrays have been conducted. The inclusion of fluorinates metal phthalocyanines in sensor arrays, together with unsubstituted phthalocyanines and/or phthalocyanines with other types of substituents, could open up broad prospects for wider use of these materials.

3.2. Solution Processed Films

Films of metal phthalocyanine bearing fluoroalkyl or fluoroaryl substituents, which are deposited by drop cast, spin coating and jet spray techniques, are also widely used as chemiresistive sensors for the detection of toxic gases such as H₂S, NO₂ or NH₃. For example, films of phthalocyanines with various fluoroalkoxy substituents were studied in a series of works [52,57,58] as active layers of chemiresistive sensors for NO₂ detection. Dong et al. [55] prepared conductive films of a metal-free H₂Pc(OCH₂CF₃)₄ derivative (Compound 8, Table 1) by a solution-based quasi-Langmuir-Shäfer (QLS) method, which demonstrated stable and reproducible responses to electron-accepting NO₂ gas in the range of 100–500 ppb at room temperature. The authors suggested that the interaction was based on weak intermolecular contacts rather than redox chemistry and the sensor response could primarily be governed by two interior NH protons of H₂Pc. They also found that no obvious change in current was observed in the reaction of H₂Pc(OCH₂CF₃)₄ with H₂S and NH₃.

Wang et al. [58] fabricated self-assembled nanostructures on the basis of H₂[Pc(OCH₂CF₃)₃] and Zn[Pc(OCH₂CF₃)₃] (Compounds 10, Table 1) by the phase transfer method. Both nanostructures demonstrated a decrease in conductivity upon exposure to electron-accepting NO₂ gas (50–900 ppb) and its increase during recovery (Figure 10, left figure), which was consistent with the sensing behavior reported previously for n-type semiconductors. The detection limit was 50 ppb and 100 ppb for the helical microribbons of H₂[Pc(OCH₂CF₃)₃] and nanowires of Zn[Pc(OCH₂CF₃)₃], respectively, depending mainly, according to the authors’ opinion, on their conductivity and ordered morphology of the resulting microstructures.

Later, Sun et al. [57] obtained similar results for thin films of fluoroalkoxy-substituted phthalocyanines with longer perfluoroalkyl chains. They investigated the effect of the method of film formation on their morphology and sensor properties and found that films consisting of more evenly distributed crystallites were formed when deposited in a vacuum compared to the drop-casted films. Vacuum deposition led to an increase in the conductivity of the films and, as a result, to the sensor response to NO₂. Both films demonstrated a linear dependence of the sensor response on the NO₂ concentration from 100 ppb to 1 ppm with a noticeable increase in sensitivity from 7.54% ppm⁻¹ for the drop-casted film to 12.05% ppm⁻¹ for the film deposited in vacuum (Figure 10, right figure).

Phthalocyanines with fluoroaryl substituents were studied as sensing layer for the detection of ammonia and NO₂. Kaya et al. [51] prepared films of a CoPc derivative bearing 5-(trifluoromethyl)-2-mercaptopyrirdine substituents (Compound 12, Table 1) and tested them as sensing layers against low concentrations of NH₃ (0.3–50 ppm) by measuring changes in the films’ conductivity at different humidities. The first oxidation potential of the prepared CoPc was higher and the reduction potential was lower compared to similar derivatives without non-fluorinated substituents, which made fluorinated phthalocyanines more sensitive to the reducing analytes. The prepared sensor had a detection limit of NH₃ 0.3 ppm, and allowed ammonia to be detected in the presence of VOCs and low concentrations of CO₂, but the presence of high CO₂ concentrations led to the distortion of the sensor response.
Figure 10. (left) Time-dependent current plots for the microribbons of H₂Pc[OCH₂C₃F₇]₈ (A) and the nanowires of Zn[Pc(OCH₂C₃F₇)₈] exposed to NO₂ at varied concentration (B). Reprinted from [58] with permission from Elsevier. (right) I-V curves measured on the drop-casted (DC) film and the film deposited in vacuum (VD) (A); the time-dependent current plot of sensor as a function of the NO₂ concentration in N₂ atmosphere for the DC film (B), and the VD film (C); and the sensor response varies linearly with NO₂ concentration of the DC film and the VD film (D). Reprinted from [57] with permission from Royal Society of Chemistry.

Duan et al. [52] tested films of a series of tetrasubstituted cobalt and metal-free phthalocyanine derivatives with 4-trifluoromethylphenoxy groups in peripheral (MPc[β-O(4-CF₃-Ph)₄]) and non-peripheral (MPc[α-O(4-CF₃-Ph)₄]) positions of phthalocyanine ring (Compounds 6, Table 1) as sensors towards NO₂, NH₃ and H₂S. They showed that the LOD of NO₂ increased in the order of CoPc[β-O(4-CF₃-Ph)₄] (3 ppb) < H₂Pc[β-O(4-CF₃-Ph)₄] (30 ppb) < CoPc[α-O(4-CF₃-Ph)₄] (198 ppb) < H₂Pc[α-O(4-CF₃-Ph)₄] (250 ppb). The maximal sensitivity of a CoPc[β-O(4-CF₃-Ph)₄] film to NO₂ was explained by the governed role of Co–NO₂ coordination strength and the best conductivity of the films of this phthalocyanine derivative. CoPc[β-O(4-CF₃-Ph)₄] films were found to exhibit the highest sensitivity and the lowest sensor response to NH₃ and H₂S. It was interesting that, upon interaction with oxidizing NO₂, all four sensors exhibited a decrease in current, behaving as n-type semiconductors. However, a positive current response was observed for CoPc[β/α-O(4-CF₃-Ph)₄] towards electron-donating NH₃, resulting from n-type charge carriers, while a negative current response was observed for H₂Pc[β/α-O(4-CF₃-Ph)₄] as a p-type material. According to the authors, that behavior was attributed to the lower levels of LUMO energies in cobalt phthalocyanines compared to the metal-free ones.

The analysis of the sensor properties of metal phthalocyanines with fluoroalkyl and fluoroaryl substituents shows that their sensor performance is determined not only by the type of substituents, but also by their position in phthalocyanine rings.

Apart from monophthalocyanines, bis- and tris(phthalocyaninato) rare earth complexes are also used for application in chemiresistive sensors, however the works on investigation of sensor properties of fluorinated bis- and tris-phthalocyanines are sporadic. Zhao et al. [82] studied the solution-based films of two ambipolar (p-fluoro)phenoxo substituted tris(phthalocyaninato) rare earth semiconductors with gadolinium Gd₂[Pc(OPhF)₈]₃ and terbium Tb₂[Pc(OPhF)₈]₃ (Compounds 11, Table 1). Both films prepared by a quasi-Langmuir-Shäfer (QLS) method revealed ambipolar semiconductor nature with a p-type response toward ammonia and n-type response toward nitrogen dioxide. The ambipolar behavior was associated not only with suitable HOMO and LUMO levels, but also with different electronic induction effects of the investigated gases. Apart from this, the films
of Tb$_2$[Pc(OPhF)$_8$]$_3$ having J-type (edge-to-edge) packing mode and, as a consequence, the larger specific surface area, displayed noticeably higher sensor response to both NH$_3$ and NO$_2$, compared to the films of Gd$_2$[Pc(OPhF)$_8$]$_3$ with a stronger intermolecular π-π stacking in the H-type (face-to-face) packing mode. Tb$_2$[Pc(OPhF)$_8$]$_3$ films exhibited stable and reversible response to NH$_3$ in the concentration range of 1–25 ppm with the LOD as low as 0.15 ppm.

Thus, the literature analysis shows that films of metal phthalocyanines bearing fluoroalkyl or fluoroaryl substituents, which are deposited by solution methods, are much less studied compared to MPcF$_x$ ones. At the same time, the chemical versatility of substituted phthalocyanines allows the introduction of various substituents, which can allow for a wide variation in the sensitivity of compounds to analytes of different nature. Moreover, the better solubility of MPcs with fluoroalkyl or fluoroaryl substitutes compared to MPcF$_x$ derivatives provides the ability to produce inks and to use inkjet printing, which offers several advantages over other methods for deposition of thin films, e.g., patterning capability, reduction in waste, high speed, low cost, applicability to large areas and flexible substrates.

### 3.3. Hybrid Materials with Carbon Nanotubes

It is known that the synergistic combination of the properties of phthalocyanines and carbon nanomaterials leads to the improvement of various properties of hybrid materials [105]. Along with other phthalocyanines, the examples of application of their fluorinated derivatives in gas sensors are also described in the literature [106]. Sharma and co-authors [63,64,83–85] prepared hybrid materials via non-covalent functionalization of acid-treated multi-walled (MWCNTs-COOH) and single-walled (SWCNTs-COOH) with MPcF$_{16}$ derivatives (Figure 11, left image).

![Figure 11](image_url)  
 (*left*) TEM images of MWCNTs-COOH (a) and ZnPcF$_{16}$/MWCNTs-COOH (b) hybrids. (*right*) (a) Response histogram of a ZnPcF$_{16}$/MWCNTs-COOH sensor for 1 ppm of Cl$_2$, NO$_2$, NO, C$_2$H$_5$OH, H$_2$S, NH$_3$ and CO at room temperature; (b) Sensor response as a function of temperature for 1 ppm of Cl$_2$ concentration; (c) Response curves of the sensor for different doses of Cl$_2$ at 150 °C; (d) Variation in the response of sensor with Cl$_2$ concentration. Reprinted from [64] with permission from Elsevier.

The sensing layers of ZnPcF$_{16}$/MWCNTs-COOH and CuPcF$_{16}$/SWCNTs-COOH hybrids were shown to have high sensitivity to Cl$_2$ with a detection limit of 0.06 ppb and 0.27 ppb, respectively, and excellent recovery and reversibility (Table 2) [63,64,85]. The response was found to be 21.28% for 2 ppm of Cl$_2$ with a response time of 14 s (Figure 11, right) for the hybrid material with ZnPcF$_{16}$.

To investigate how central metal affects the interactions between the phthalocyanine and single-walled carbon nanotubes and gas sensing properties of the prepared hybrids, the same group of authors investigated MPcF$_{16}$ with M = Co, Zn, and Cu [85]. The results...
demonstrated that the response decreased in the order of Co > Zn > Cu, indicating that the central metal ions play an important role in the sensitivity to Cl₂. CoPcF₁₆/SWCNTs–COOH sensor exhibited the highest sensitivity (82% for 2 ppm with LOD of 0.04 ppb), excellent reproducibility and selectivity towards chlorine (Figure 12).

In our recent paper [86], the sensor response of the layers of hybrid materials of single-walled carbon nanotubes noncovalently functionalized with a fluoroalkyl substituted zinc(II) phthalocyanine (Compound 7, Table 1) was compared with that of the similar hybrid modified with the nonfluorinated analogue to reveal the role of fluorinated substituents. It was found that the introduction of long fluoroalkyl substituents led to a decrease in the functionalization degree; the amount of ZnPc-CF molecules adsorbed on SWCNT walls was 1.5 times less than in the case of the hybrid modified with the nonfluorinated phthalocyanine (ZnPc-CH). As a result, the sensitivity of ZnPc-CF-based sensor to ammonia was two times less than in the case of SWCNT/ZnPc-CH, while its sensor response was more stable in a humid atmosphere (RH 70%) (Figure 13).

These few examples show that hybrids of fluorinated phthalocyanines with carbon nanomaterials (e.g., SWCNT, MWCNT and graphene derivatives) are also promising materials as active layers of chemiresistive layers. The use of hybrid materials leads to an increase in the conductivity of the sensitive layers, which avoids the use of expensive highly sensitive electrometers, but the selectivity of hybrid-based sensors becomes less than in the case of pure phthalocyanine films. At the moment, the limited number of studied hybrid materials with fluorinated phthalocyanines does not allow us to make any conclusions...
about any correlations between their structure and sensor properties. Expanding the range of fluorinated substituents in the phthalocyanine ring and obtaining hybrids by covalent functionalization of nanotubes with fluorinated phthalocyanines may be a further way to develop this scientific direction and improve the performance of sensor devices.

4. Other Types of Chemical Sensors

Apart from the sensors with electrical sensor response, the films of fluorinated metal phthalocyanines are utilized in other types of chemical sensors. Among them, the most popular are optical sensors and quartz crystal microbalance (QCM) ones (Table 3).

Table 3. Main characteristics of optical and QCM sensors on the basis of fluorinated metal phthalocyanines.

| Active Layer | Sensor Type | Analyte | Investigated Range, Ppm | LOD, Ppm | Recovery Time, S | Ref. |
|--------------|-------------|---------|-------------------------|----------|-----------------|------|
| MPcF_{16} (M = Zn, Co, Cu, Ni) | SPR | NH₃ | 100, 200 ppm | n/a | 15–30 | [96] |
| CoPCF_{16} | TIRE | NH₃ | 50–1000 | n/a | n/a | [107] |
| ZnPc(OCH₂CF₂CH₂F)₈ (Compound 13, Table 1) | TIRE | Trimethylamine | 10–300 | 20 | n/a | [56] |
| MPcF_{16c} (M = Zn, Cu) | QCM | Toluene | 500 | n/a | n/a | [108] |

- **TILR₄ (Compounds 14, Table 1)** (See Section 4.2.)

- **Compounds 15, Table 1**

- **Compounds described in Section 4.2.**

| Active Layer | Sensor Type | Analyte | Investigated Range, Ppm | LOD, Ppm | Recovery Time, S | Ref. |
|--------------|-------------|---------|-------------------------|----------|-----------------|------|
| MeOH | QCM | Toluene | 1000–5000 | 130–650 | 0.6 (for 1b) | [109] |
| n-Propanol | | | 900–4500 | 10–50 | 0.8 (for 2c, see Section 4.2.) | |
| Ethyl acetate | | | 950–4700 | 3–15 | 40 (for 1b) | |
| Diethylenetriamine | | | 380–1900 | 70–350 | | |
| Acetonitrile | | | 240–1200 | 40–200 | | |
| DMMP | | | 150–730 | 100–480 | | |
| n-Heptane | | | 100–480 | 150–730 | | |
| Ethylbenzene | | | 380–1900 | 721–3606 | | |
| Tolueno | | | 788–3939 | 721–3606 | | |
| o-Xylene | | | 385–1927 | 721–3606 | | |
| p-Xylene | | | 10,030 | 788–3939 | | |
| Chlorobenzene | | | 60 | 100–480 | | |
| Chloroform | | | 44 | 100–480 | | |
| Dichloromethane | | | 34 | 100–480 | | |
| Toluene | | | 58 | 100–480 | | |
| Chloroform | | | 36 | 100–480 | | |
| Trichloroethylene | | | 13 | 100–480 | | |
| Acetonitrile | | | 114 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Propanol | | | 3 | 100–480 | | |
| Methanol | | | 2 | 100–480 | | |
| Ethanol | | | 3 | 100–480 | | |
| Methanol | | | 144 | 100–480 | | |
| Propanol | | | 13 | 100–480 | | |
| Acetonitrile | | | 58 | 100–480 | | |
| Ethanol | | | 36 | 100–480 | | |
| Toluene | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |
| Ethanol | | | 3 | 100–480 | | |
| Toluene | | | 144 | 100–480 | | |
| Ethanol | | | 13 | 100–480 | | |
| Methanol | | | 58 | 100–480 | | |
| Propanol | | | 36 | 100–480 | | |
| Acetonitrile | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 144 | 100–480 | | |
| Ethanol | | | 13 | 100–480 | | |
| Methanol | | | 58 | 100–480 | | |
| Propanol | | | 36 | 100–480 | | |
| Acetonitrile | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 144 | 100–480 | | |
| Ethanol | | | 13 | 100–480 | | |
| Methanol | | | 58 | 100–480 | | |
| Propanol | | | 36 | 100–480 | | |
| Acetonitrile | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 144 | 100–480 | | |
| Ethanol | | | 13 | 100–480 | | |
| Methanol | | | 58 | 100–480 | | |
| Propanol | | | 36 | 100–480 | | |
| Acetonitrile | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 144 | 100–480 | | |
| Ethanol | | | 13 | 100–480 | | |
| Methanol | | | 58 | 100–480 | | |
| Propanol | | | 36 | 100–480 | | |
| Acetonitrile | | | 13 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Toluene | | | 3 | 100–480 | | |
| Ethanol | | | 2 | 100–480 | | |
| Methanol | | | 3 | 100–480 | | |
| Propanol | | | 2 | 100–480 | | |
| Acetonitrile | | | 3 | 100–480 | | |

4.1. Optical Sensors

Surface plasmon resonance (SPR) [96] and spectroscopic ellipsometry in total internal reflection configuration (TIRE) [56] were known to be used as optical techniques to study the sensor response of thin layers of fluorinated phthalocyanine derivatives. In our previous work [96], an SPR technique in the Kretschmann configuration was utilized for
the investigation of the sensor response of MPcF\textsubscript{16} (M = Zn, Co, Cu, Ni) films deposited on gold-coated glass substrates to ammonia at 100 and 200 ppm. This is a well-known optical method for real-time monitoring of various molecular interactions (binding), their mechanisms and kinetics. The sensor response is based on the changes in the refractive index of the sensing layer, caused by the binding between an analyte in gas or solution, due to the generation of the surface plasmons at a metal/dielectric interface in a specific condition. The typical SPR curves, which are the dependence of reflected light intensity on the internal angle of incidence, are shown in Figure 14 (left graph) for the pure gold-coated substrate (a), the thin film of as-deposited CuPcF\textsubscript{16} (b), and the film exposed to ammonia (c). The kinetic curves of the sensor response of the MPcF\textsubscript{16} thin films to NH\textsubscript{3} (100 and 200 ppm) are presented in Figure 14 (right graph).

It was found that the sensor response decreased in the order ZnPcF\textsubscript{16} > CoPcF\textsubscript{16} ≥ CuPcF\textsubscript{16} > NiPcF\textsubscript{16}. To obtain more insight into the interplay between microscopic structure and sensor response of the films, the authors carried out the DFT calculations of the binding energies of phthalocyanines with analyte molecules, and measured a shift of the selected IR bands in MPcF\textsubscript{16} spectra during the exposure to gaseous ammonia. It was shown that the energies of MPcF\textsubscript{16} · NH\textsubscript{3} complex formation, red shifts of wavenumbers of some IR bonds, and refractive index changes appearing upon exposure ammonia correlated well with each other.

A total internal reflection ellipsometry method (TIRE) was also employed as an optical technique to examine CoPcF\textsubscript{16} as an optical active layer for the detection of ammonia [107] and zinc phthalocyanine with fluorinated n-propanol in peripheral positions (Compound 13, Table 1) as an active layers for the detection of trimethylamine [56]. TIRE combines the spectroscopic ellipsometry platform with the Kretschmann’s SPR geometry [112]. The experimental setup and principles of this method are described in more detail in earlier publications [113,114]. The spectrum of $\Psi(\lambda)$, which exhibits the amplitude ratio of $A_p/A_s$ between $p$- and $s$-components of polarized light, is similar to the conventional SPR curve, while the spectrum of $\Delta(\lambda)$ is associated with the phase shift between $p$- and $s$-components. According to Arwin’s modelling [112], the position of the sharp drop in the $\Delta(\lambda)$ spectrum is about 10 times more sensitive to adsorption of analyte molecules than the $\Psi(\lambda)$ spectrum.

![Figure 14. (left) Surface plasmon resonance curves for (a) pure gold-coated substrate; (b) gold/as-deposited CuPcF\textsubscript{16} film; and (c) gold/CuPcF\textsubscript{16} exposed by NH\textsubscript{3} gas (200 ppm). (right) SPR response curves of MPcF\textsubscript{16} thin films toward gaseous NH\textsubscript{3} (100 ppm and 200 ppm, respectively): (a) NiPcF\textsubscript{16}, black; (b) CuPcF\textsubscript{16}, red; (c) CoPcF\textsubscript{16}, blue; (d) ZnPcF\textsubscript{16}, green. The SPR response curves were recorded using the wavelength of 633 nm (He–Ne laser) at a fixed angle of incidence $\Theta = 44.2$. Reprinted from [96] with permission from Elsevier.]

![Graph showing SPR curves for different samples and SPR response curves for MPcF\textsubscript{16} thin films towards gaseous NH\textsubscript{3}.](image-url)
TIRE spectra of the spun films of ZnPc(OCH\(_2\)CF\(_2\)CHF\(_2\))\(_8\) (Compound 13, Table 1), and its nonfluorinated analogue ZnPc(OCH\(_2\)CH\(_2\)CH\(_3\))\(_8\), before and after exposure to trimethylamine are shown in Figure 15 as an example [56]. The change in the \(\Delta(\lambda)\) spectrum is much more pronounced than in the case of the \(\Psi(\lambda)\) spectrum. The change in the optical parameters (Table 4) of the ZnPc(OCH\(_2\)CF\(_2\)CHF\(_2\))\(_8\) film and as a consequence its optical response was found to be higher than for the film of nonfluorinated derivative. It was shown that, similarly to the case of chemiresistive sensors, the optical response was higher in the case of derivatives bearing fluorinated substituents, and the limit of trimethylamine detection was 20 ppm.

![TIRE spectra](image)

**Figure 15.** (a) \(\Psi(\lambda)\) and \(\Delta(\lambda)\) TIRE spectra: (a) ZnPc(OCH\(_2\)CH\(_2\)CH\(_3\))\(_8\) in air (curve 1); after injection of trimethylamine 200, 250 and 300 ppm (curves 2, 3 and 4, respectively); after flushing with air (curve 5); (b) the film of ZnPc(OCH\(_2\)CF\(_2\)CHF\(_2\))\(_8\) in air (curve 1); after injection of trimethylamine 20, 60, 100, 250 and 300 ppm (curves 2–6, respectively); after flushing with air (curve 7). Enlarged sections of \(\Delta(\lambda)\) spectra are shown on the top. Reprinted from [56] with permission from Elsevier.

**Table 4.** Thickness (d), refractive indexes (n) and extinction coefficients (k) for ZnPc(OCH\(_2\)CH\(_2\)CH\(_3\))\(_8\) and ZnPc(OCH\(_2\)CF\(_2\)CHF\(_2\))\(_8\) films, before and after interaction with trimethylamine [56].

|                   | ZnPc(OCH\(_2\)CH\(_2\)CH\(_3\))\(_8\) | ZnPc(OCH\(_2\)CF\(_2\)CHF\(_2\))\(_8\) |
|-------------------|--------------------------------------|--------------------------------------|
|                   | Initial Film                         | After Exposure with Trimethylamine   |
|                   |                                      | Initial Film                         | After Exposure with Trimethylamine |
|                   | n (\(\lambda = 633\) nm)            | 1.33                                 | 1.33                                 |
|                   | k (\(\lambda = 633\) nm)            | 0.15                                 | 0.15                                 |
|                   | d, nm                                | 19.4                                 | 19.7                                 |

The authors of [105] used a TIRE method to compare the sensor response of CoPcF\(_{16}\) films deposited at different substrate temperatures to ammonia. They found that the films deposited at a substrate temperature of 220 °C exhibited the higher response, due to their greater roughness and more developed surface [96,107].

In comparison to chemiresistive sensors, the optical ones on the basis of fluorinated MPcs exhibit less sensitivity to investigated analytes. One of the possibilities for improving their sensitivity is related to their supramolecular organization on the substrate surface. For example, the preparation of nanostructured films in the form of nanofibers and nanowires with a developed surface area [115] would increase the sensitivity of the sensor layers.

### 4.2. Quartz Crystal Microbalance Sensors

One more method, in which fluorinated phthalocyanines are used as sensing materials, is quartz crystal microbalance (QCM). QCM is an analytical tool sensitive to mass
changes on the surface. Its principle of operation is based on the change in the mass of the active substance on the surface of the converter during gas adsorption, which leads to a change in the resonant frequency of the crystal in accordance with the Sauerbrey’s equation [116]. QCM sensors based on phthalocyanines, including fluorinated ones, were used for detection of various analytes. For example, Kumar and co-workers [108] compared the sensitivity of MPcF_{16} (M = Cu, Zn)-coated QCMs to toluene with that of the corresponding unsubstituted and tert-butyl-substituted derivatives. It was shown that the introduction of fluorine atoms decreased the sensitivity of metal phthalocyanines to toluene.

Harbeck et al. [109] tested a series of metal phthalocyanines bearing fluoroalkyloxy substituents (Compounds 15, Table 1), which exhibited a good sensor performance toward some volatile organic compounds (VOCs), both gaseous and dissolved in water. All sensors demonstrated reversible sensor response to VOCs at room temperature and a linear dependence on analyte concentrations (Figure 16).

Figure 16. Transient signal of a QCM sensor with the film of octasubstituted CuPc derivative (Compound 15c, Table 1) during exposure to samples containing o-xylene in concentration between 1 and 20 ppm (a) and resulting calibration curve (b). Reprinted from [109] with permission from Elsevier.

It was shown that the sensor response increased for all materials in the order dichloromethane < chloroform < toluene < chlorobenzene < tetrachloroethylene < p-xylene < o-xylene. The maximal response was observed for octasubstituted phthalocyanine (Compound 15c, Table 1) with the LOD of dichloromethane of 5 ppm and the LOD of o-xylene of 0.05 ppm.

Phthalocyanines with similar fluoroalkyloxy-substituents as well as with fluoroaryloxy-groups were studied in QCM sensors toward another set of volatile organic compounds (methanol, propanol, acetonitrile, ethyl acetate, toluene, o-xylene, chlorobenzene, eriethylamine etc.) [33]. Octasubstituted NiPc and ZnPc with fluoroalkyloxy groups, which increase their polarity and polarizability, demonstrated the best sensor performance and were shown to be very sensitive to polar compounds such as ethyl acetate or acetoni-
trile. LODs, except for methanol, were below 100 ppm, and for some aromatic VOCs, even below 10 ppm.

Similar tetra- and octasubstituted titanium phthalocyanines with -O-CH$_2$CF$_2$CHF$_2$ groups in the benzene rings and different axial substituents (Compounds 14, Table 1; Figure 17(1)) were tested as QCM sensors toward dimethyl methylphosphonate (DMMP), MeOH, n-propanol, ethyl acetate, triethylamine, acetonitrile and their mixtures [54]. The principal component analysis (PCA) was used to treat the data on investigation of their sensor response (Figure 17(2)). It was shown that, along with substituents in the phthalocyanine ring, the type of the axial ligand had a pronounced effect on both sensor response and selectivity to investigated analytes. The best value of the sensor response to dimethyl methylphosphonate and fast kinetics were found for 1f and 2f compounds (Figure 17(1)). 1f and 1g, as well as 2e and 2f, derivatives exhibited the best sensor response to triethylamine.

Figure 16. Transient signal of a QCM sensor with the film of octasubstituted CuPc derivative (Compound 15c, Table 1) during exposure to samples containing o-xylene in concentration between 1 and 20 ppm (a) and resulting calibration curve (b). Reprinted from [109] with permission from Elsevier.

The increased affinity of fluorinated phthalocyanines for polar compounds makes them very suitable for sensors for polar DMMP and other organophosphate compounds. Eleven different ZnPc and NiPc with different fluorinated substitutions (Figure 18a) were used to study the sensor response to DMMP by QCM and surface acoustic wave (SAW) methods, in order to choose compounds with the best sensor response [110]. It was shown that the sensor response is influenced by the central metal, but to a much greater extent by the nature and number of substituents. For this reason, all factors must be taken into account when choosing compounds with the best sensor properties. Among the studied compounds, the best sensor response to DMMP, measured by a QCM technique, was observed for the derivatives 1b and 2c (Figure 18b) with the calculated LOD of 0.6 ppm and 0.8 ppm, respectively. Interestingly, the sensitivity of the same compounds to DMMP, studied by a SAW technique, was different (Figure 18c), which the authors explained by the viscoelasticity of the materials and the inhomogeneity in the sensing layers. The compound 1b had also the best sensor response to DMMP, but the response value for 2c was less, and was comparable with other investigated phthalocyanine derivatives. In the case of 1b, LOD was as low as 50 ppb both in dry and humid air.
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Figure 18. Chemical structures of phthalocyanines with R and R′ substituents (a). DMMP sensitivities of phthalocyanines having fluorinated and non-fluorinated substituents as obtained with QCM sensors in dry air (b) and SAW sensitivities (c) for the selected compounds. Adapted from [110] with permission from Elsevier.

Ahmetali et al. [111] studied relative humidity sensing performance of fluoro-substituted asymmetric zinc phthalocyanines substituted with 3-hydroxy-3-methyl-1-butynyl, ethynyl, and 4-nitrophenylethynyl (Compounds 16, Table 1) films, using quartz crystal microbalance (QCM). Results indicated that the value of sensor response and the response and recovery times strongly depended on the thickness of the sensor layer, and the best characteristics were obtained at the film thickness of 450 nm. The most useful sensor for the determination of relative humidity was found to be the film of peripherally substituted unsymmetrical ZnPc bearing nitrophenyl group (Compound 16c, Table 1).

Thus, the use of QCM sensors based on fluorinated phthalocyanines makes it possible to detect not only oxidizing and reducing gases, but also VOCs, which play a critical role in food quality control [117], explosives detection [118], and medical diagnostics [119]. The creation of E-noses, or cross-reactive sensor arrays on the basis of fluorinated phthalocyanines, together with MPcs bearing other types of substituents, could open up broad prospects for wider use of these materials for the detection of important analytes in gas mixtures.

5. Conclusions

An overview of the current state of research in the field of applications of fluoro-substituted metal phthalocyanines as active layers of gas sensors was provided in this review. The literature analysis shows that both phthalocyanines with fluorine atoms directly in the aromatic rings and phthalocyanines bearing fluoroalkyl and fluoroaryl substituents are widely used for the preparation of active layers of gas sensors. In these
compounds, fluorine demonstrates electron-withdrawing effects, molecule stability, and enhanced chemical interactions.

In most publications, fluorinated phthalocyanines are usually compared with their non-fluorinated counterparts to observe the degree of improvement in sensor properties. Perfluorination and the introduction of some fluoroalkyl and fluoroaryl groups lead to a decrease in HOMO and LUMO energy levels, facilitating electron injection. In addition, the introduction of F-substituents into the phthalocyanine aromatic rings causes an increase in charge carrier mobilities, thus improving the performance of sensing devices. Apart from this, fluorine substituents decrease the electron density of the aromatic ring and increase the oxidation potential of the MPc molecule. As a result, fluoro-substituted phthalocyanines exhibit a higher sensor response to reducing gases such as ammonia.

Thin films of MPcF\textsubscript{x} (M = Cu, Co, Zn, Pb, Pd VO; x = 4, 16) derivatives have already been systematically investigated as active layers for ammonia detection. It was shown that among investigated MPcF\textsubscript{x}, phthalocyanines of cobalt and zinc demonstrated the best sensing performance, with the limit of NH\textsubscript{3} detection reaching 0.1 ppm in the case of CoPcF\textsubscript{4} and ZnPcF\textsubscript{4} films. A similar tendency was also observed in the case of SPR sensors. They can be used for the selective detection of NH\textsubscript{3} in the presence of some reducing gases and volatile organic compounds, namely carbon dioxide, acetone, dichloromethane and ethanol, and even at high humidity. These properties make MPcF\textsubscript{x} films good candidates for future applications as sensors for detecting ammonia in exhaled air, which is known to be a biomarker of renal failure in nephritis, atherosclerosis of the renal arteries, toxic lesions, and other kidney diseases.

Sensing layers of phthalocyanines bearing fluoroalkyl or fluoroaryl moieties are less investigated than MPcF\textsubscript{x}, and questions about the effect of the number and the type of fluorine-containing substituents on the sensor performance have not been sufficiently answered, and may be the subject of future research, although some regularities can be noted. At the same time, the chemical versatility of substituted phthalocyanines allows the introduction of various substituents, which can allow for a wide variation in the sensitivity of compounds to analytes of different nature. Moreover, the better solubility of MPcs with fluoroalkyl or fluoroaryl substitutes compared to MPcF\textsubscript{x} derivatives provides the ability to produce inks and to use inkjet printing, which offers several advantages over other methods for the deposition of thin films. Similarly to MPcF\textsubscript{x}, chemiresistive sensors based on MPcs with fluoroalkyl and fluoroaryl substituents demonstrate high sensitivity to ammonia with the detection limit up to 0.15–0.3 ppm. They were also shown to demonstrate quite good electrical response to NO\textsubscript{2} with the detection limit of tenths of ppm.

QCM sensors based on MPcs with fluoroalkyl and fluoroaryl substituents are good candidates for the detection of volatile organic compounds, which play a critical role in food quality control, explosives detection, and medical diagnostics. Their octasubstituted derivatives demonstrate the better sensor performance in comparison with their tetrasubstituted analogues, and they are shown to be very sensitive to dimethyl methylphosphonate aromatic hydrocarbons with a detection limit at the ppb level.

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