



Article

Thin Films of Chlorinated Vanadyl Phthalocyanines as Active Layers of Chemiresistive Sensors for the Detection of Ammonia

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Abstract: Halogenated metal phthalocyanines are promising materials for the manufacture of active layers of chemiresistive sensors for the detection of various gases. Despite the high interest in such sensors, there are few systematic studies of the position of halogen substituents in phthalocyanine macroring on the chemiresistive response of their films to gases. In this work, we prepared and studied films of novel tetrachlorosubstituted vanadyl phthalocyanine derivatives with Cl substituents in the peripheral (VOPcCl₄-p) and nonperipheral (VOPcCl₄-np) positions of the phthalocyanine ring as active layers of chemiresistive sensors to reveal the effect of the position of substituents on their structure and sensor response to low concentrations of NH₃. It was shown that the films of VOPcCl₄-p exhibited a noticeably higher sensor response to NH₃ than the VOPcCl₄-np ones. The limit of detection of NH₃ was 0.7 ppm. The sensing layers demonstrated a reversible sensor response at room temperature with fairly low response/recovery times. It was also demonstrated that NH₃ can be detected in the presence of various interfering gases (CO₂ and H₂) and some volatile organic vapors, as well as in a mixture of gases with a composition close to exhaled air.

Keywords: vanadyl phthalocyanines; chemiresistive sensors; gas sensors; ammonia



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1. Introduction

Ammonia is a colorless gas with a specific smell. The main consumers of ammonia are agricultural enterprises, although it is also used in various household and industrial cleaning products, as well as in industrial metalworking processes, the paper industry, and industrial refrigeration units [1]. Ammonia has a strong corrosive effect and causes severe irritation of the skin, eyes, mucous membranes of the mouth, and respiratory and digestive systems [2]. Its concentration above 100 ppm can cause burning in the eyes, lacrimation, swelling of the eyelids, corneal abrasion, blurred vision, and even blindness. The detection of ammonia is an important task not only in industry but also in medicine [3,4]. Ammonia is used as a biomarker for the diagnostics of disease by analyzing its content in breath air. For example, an increased level of NH₃ in exhaled air of more than 2 ppm is a sign of renal pathologies [5,6].

Currently, electrochemical and luminescent sensors, as well as gas chromatography–mass spectrometry are most often used to analyze these gases in exhaled air [7–9]. The development of new semiconductor sensors for the analysis of gas biomarkers is of particular interest due to their cheapness, portability, and speed. Oxides [10,11], transition metal nitrides [12,13], nanocarbon-containing materials [14], and metal phthalocyanines [4,15,16] are widely used as active layers of chemiresistive sensors. The latter attract attention due to the possibility of widely varying their resistive and electrocatalytic properties by changing their molecular structure (e.g., central cations and substituents in the macroring or axial

positions), as well as the morphology and orientation of their films. Another advantage of MPc layers is the reversibility of their response at room temperature without additional heating, as well as the possibility of creating sensing layers on flexible substrates [17–19].

Among the variety of metal phthalocyanines, phthalocyanines with various substituents in axial positions can be distinguished, for example, phthalocyanines of gallium and aluminum MXPc ($M = \text{Al, Ga}$; $X = \text{Cl, OH, F}$), as well as phthalocyanines of titanyl and vanadyl (TiOPc and VOPc). Such phthalocyanines have a packaging type different from phthalocyanines $M(\text{II})\text{Pc}$ ($M = \text{Mg, Cu, Co, Ni}$), as they have a flat structure and additional places of interaction with gas analytes [20,21]. For instance, unlike other 3D-metal phthalocyanines, VOPc and its substituted derivative, VOPcR_n ($n = 4, 8, 16$), are nonplanar molecules with vanadyl groups located perpendicular to the plane of aromatic rings [22,23]. This leads to two-dimensional π - π stacking in the crystal lattice and, as a consequence, to shorter intermolecular distances and greater overlap of the π - π stacking compared to planar phthalocyanines, which ultimately contributes to the higher mobility of charge carriers [24]. These properties open up the prospect of using them in highly productive organic thin-film field-effect transistors (OFETs) and sensors.

Ultrathin vanadyl phthalocyanine films were used as sensing layers of chemiresistors for the detection of nitrogen dioxide at room temperature [25]. Surface-type capacitive humidity sensors based on evaporated VOPc films were studied by two different groups of authors [26,27]. Ji, et al. [28] fabricated an ultra-thin highly ordered heterojunction-structured device based on multilayers of VOPc, N,N' -diphenyl perylene tetracarboxylic diimide (PTCDI-Ph), and para-hexa-phenyl (p-6P), which was very sensitive to NO_2 and had a nearly five times larger response than the corresponding single-heterojunction device.

Many authors show in their works that the introduction of halogen substitutes into the phthalocyanine macrocycles results in improvements in their sensitivity to electron-donating gases [29,30]. In tetrasubstituted phthalocyanine molecules, halogen substituents can be introduced into both peripheral ($\text{MPcX}_4\text{-p}$) and nonperipheral ($\text{MPcX}_4\text{-np}$) positions of the phthalocyanine macroring (Figure 1). In our previous work, thin films of unsubstituted and tetrafluorosubstituted vanadyl phthalocyanine derivatives (VOPc and $\text{VOPcF}_4\text{-p}$) were used for the detection of gaseous ammonia and hydrogen. It was shown that $\text{VOPcF}_4\text{-p}$ films demonstrated a 2–3 times higher sensor response to NH_3 compared to VOPc films [31]. In turn, a comparative analysis of the sensor response to ammonia showed that the films of $\text{VOPcF}_4\text{-p}$ exhibited a greater sensor response than those of $\text{VOPcF}_4\text{-np}$ [32]. This result correlated well with DFT calculations, which revealed stronger binding of NH_3 and $\text{VOPcF}_4\text{-p}$ molecules.

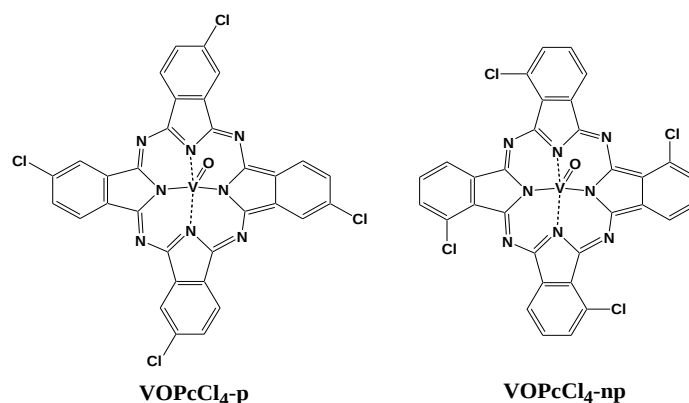


Figure 1. Vanadyl phthalocyanines with Cl substituents in the peripheral ($\text{VOPcCl}_4\text{-p}$) and nonperipheral ($\text{VOPcCl}_4\text{-np}$) positions of phthalocyanine macrocycle.

It was shown using the example of zinc phthalocyanines that films of chlorosubstituted metal phthalocyanines demonstrated an even higher chemiresistive sensor response to ammonia than fluorinated ones [30], but the structure and sensor properties of chlorosubstituted oxometallo phthalocyanine films have not yet been studied.

In this work, we prepared and studied films of novel tetrachlorosubstituted vanadyl phthalocyanines with Cl substituents in the peripheral (VOPcCl₄-p) and nonperipheral (VOPcCl₄-np) positions of the phthalocyanine ring (Figure 1) as active layers for detecting low concentrations of NH₃ and compared their sensor performance with their fluorinated analogs. The novelty of this work consists of expanding the set of metal phthalocyanines suitable for use as sensor layers and revealing the influence of the position of substituents in the macroring on the structure of films and the sensor response to the gaseous analytes. The sensor characteristics of the sensors (viz reversibility, limit of detection, response, and recovery times) were determined. The sensing layers were tested in the presence of various interfering gases (CO₂ and H₂) and some volatile organic vapors, as well as in a mixture of gases simulating exhaled air.

2. Materials and Methods

2.1. Preparation and Characterization of Thin Films

VOPcCl₄-p and VOPcCl₄-np were synthesized according to the standard template synthesis method by melting the mixture (1:4 molar ratio) of VOCl₃ with corresponding 4-chlorophthalonitrile (abcr, CAS 17654-68-1) or 3-chlorophthalonitrile (abcr, CAS 76241-79-7). The compounds were purified by vacuum sublimation (10^{−5} Torr, 420–450 °C). Thin films of VOPcCl₄-p and VOPcCl₄-np were deposited by a physical vapor deposition method, using a vacuum universal station VUP-5M (Sumy, Ukraine). The residual pressure was 10^{−5} Torr, the evaporation temperature was 420–450 °C, and the substrate temperature was about 60 °C.

Thicknesses of the VOPcCl₄-p and VOPcCl₄-np films were 82 and 87 nm, respectively. The choice of film thickness was based on preliminary studies. It was previously shown that films of smaller thickness often do not form a continuous film on the surface of the electrodes, which prevents their good conductivity. Films with a thickness of more than 100 nm have low sensor sensitivity and a long response time due to the difficulty of gas diffusion into the film. The thickness of the films was determined through spectroscopic ellipsometry, using a spectroscopic ellipsometer ELLIPS 1771 SA (ISP, Novosibirsk, Russia) according to the previously described technique [33].

An XRD analysis of VOPcCl₄-p and VOPcCl₄-np single crystals was performed using A Bruker D8 Venture (Bruker AXS Inc., Billerica, MA, USA) single-crystal diffractometer (Photon III C14 CPAD detector, MoK α Incoatec I μ S 3.0 microfocus X-ray source, 3-circle kappa-goniometer). The temperature of the crystals was 150 (1) K and was controlled using an open-flow nitrogen cooler (Cryostream 800 plus, Oxford Cryosystems, Oxford, UK). Several standard ω -scans with a frame width of 0.5° were used to collect the data. Data collection, reduction, absorption correction, and global unit cell refinement were performed in the APEX 3 [34] software package (V2018.7–2 (SAINT 8.38A, SADABS–2016/2), Madison, WI, USA). Reduced hklF datasets were then processed in Olex2 1.5 software [35] and with SHELXT v.2018/2 for the initial structure solution [36] and with SHELXL v.2018/3 [37] for the subsequent refinement. Finalized CIF files were deposited to The Cambridge Crystallographic Data Center (CCDC) with the numbers 2267526, 2267527, and 2267528 and can be obtained free of charge at www.ccdc.cam.ac.uk/structures, accessed on 5 June 2023.

An XRD study of thin films and bulk powders of VOPcCl₄-p and VOPcCl₄-np was performed using a Bruker D8 Advance powder diffractometer (Bruker AXS Inc., Billerica, MA, USA) in the Bragg–Brentano scheme with a vertical θ – θ goniometer (CuK α sealed tube, 0.01° scan step).

AFM images of the films were obtained using the Ntegra Prima II nanolaboratory (NT-MDT, Moscow, Russia). The HA_{NC} probe parameters were described in our previous work [30]. A scanning electron microscope (JEOL–JSM 6700 F, Tokyo, Japan) was used for the characterization of the films' surface morphology.

Optical absorption spectra were recorded with (OKB SPECTR LLC, Saint-Petersburg, Russia), while Raman spectra were obtained using a LabRAM Horiba single spectrometer (Montpellier, France) (488 nm line of an Ar⁺ laser).

2.2. Measurements of the Sensor Response

The chemiresistive response of VOPcCl₄-p and VOPcCl₄-np films was investigated by measuring the change in resistance upon the introduction of ammonia in the concentration range of 1–50 ppm. The resistance was measured at the constant voltage of 10 V, using an electrometer Keithley 236 (Tektronix Inc., Beaverton, OR, USA). To measure the sensor response, ammonia of the required concentration and air used for purging were alternately injected into the flow cell. Most of the experiments were conducted in dynamic mode. In this mode, ammonia was injected at a constant flow rate of 300 mL/min. The exposure time was 15 s. Static mode was used only to determine the response and recovery times of the sensors. In static mode, the airflow was passed through the chamber until the film resistance reached a constant value, and then the chamber valves were closed and NH₃ of the required concentration was injected into the cell. The resistance was recorded after the saturation current was reached. After that, the chamber was opened and blown by a stream of air. All measurements were carried out at room temperature (22 ± 2 °C).

The sensor response values were calculated: $(R - R_0)/R_0$. (R is the steady resistance of the film at a certain analyte concentration, and R_0 is the initial resistance of the film in air). The measurements of the response of three deposited films were used to calculate the standard deviation. The source of NH₃ was a tank with pure commercial (“Chistye Gasy+”, Novosibirsk, Russia) gas (1%) diluted in dry argon. The required gas concentrations were set using the mass flow controllers. Dry air was used as a diluting and purging gas.

2.3. Theoretical Calculations

The quantum-chemical approaches used here for the calculations of the geometric and electronic structures and total energies of VOPcCl₄-p/NH₃- x and VOPcCl₄-np/NH₃- y aggregates, where $x = 1-4$ and $y = 2-4$, have already been described in our previous work when performing a similar study of the interaction of ammonia molecule with fluorosubstituted phthalocyanines VOPcF₄-p and VOPcF₄-np [32]. The values of x and y specify the position of the NH₃ molecule relative to the macrocycle (Figures 2 and 3). From this point of view, the VOPcCl₄-np/NH₃-1 aggregate was not considered because it was shown [32] that such an arrangement of the molecule over the phthalocyanine plane cannot be realized due to the small distance between two adjacent macrocycles in the stack of molecules.

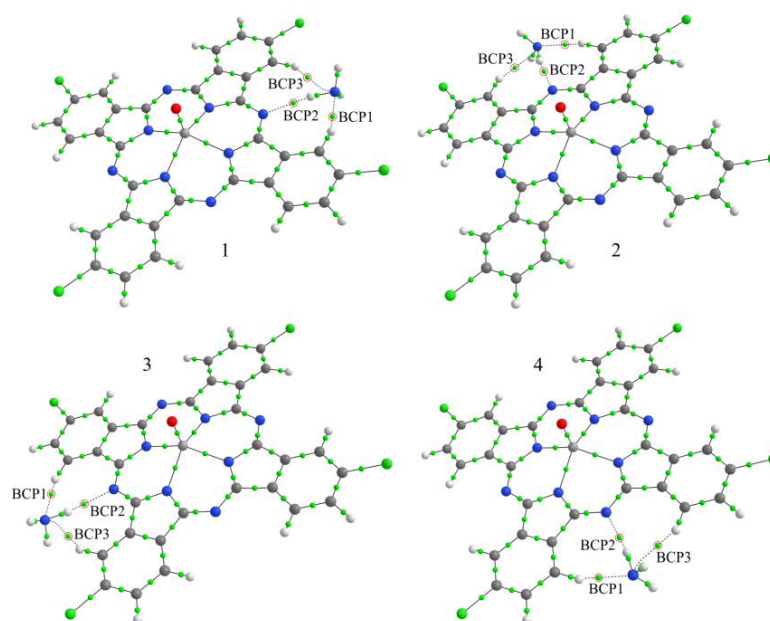


Figure 2. Structure of VOPcCl₄-p/NH₃- x (where $x = 1-4$) aggregates and bond critical points (BCPs, small green balls) in them. BCPs characterizing the interaction between the ammonia molecule and phthalocyanine atoms are shown in red circles.

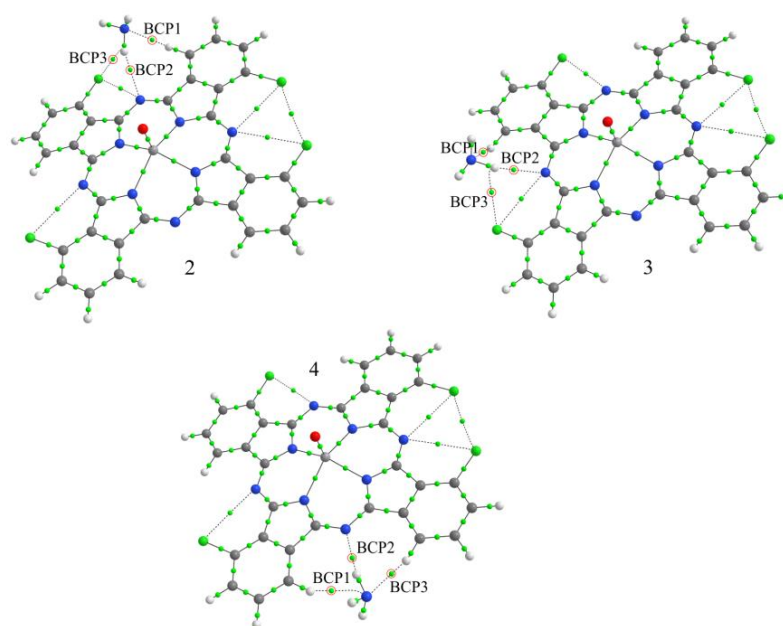


Figure 3. Structure of $\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-}y$ (where $y = 2\text{--}4$) aggregates and bond critical points (BCPs, small green balls) in them. BCPs characterizing the interaction between the ammonia molecule and phthalocyanine atoms are shown in red circles.

3. Results and Discussion

3.1. Crystal Structure of $\text{VOPcCl}_4\text{-p}$ and $\text{VOPcCl}_4\text{-np}$

Establishing the structure of single crystals is a necessary step before studying the structural features of thin films. Single crystals of vanadyl phthalocyanines were grown by sublimation in vacuum. Two types of single crystals were isolated from the $\text{VOPcCl}_4\text{-p}$ powder. Crystals in the form of very thin translucent greenish-blue ribbons were tetragonal, while needle-like crystals with a dark purple metallic sheen were in a triclinic phase. The molecular structure and packing diagrams for both $\text{VOPcCl}_4\text{-p}$ crystal phases are shown in Figure 4. Unit cell parameters and refinement details for VOPcCl_4 crystal structures are summarized in Table 1. Due to the axial oxygen atom, the $\text{VOPcCl}_4\text{-p}$ molecule is not flat and has the shape of a “shuttlecock”, while the vanadium atom is displaced from the plane of the macrocycle by 0.399 Å, and the $\text{V}=\text{O}$ bond is oriented perpendicular to the plane of the macrocycle (Figure 4a). Since $\text{VOPcCl}_4\text{-p}$ contains a mixture of regioisomers with peripheral chlorine atoms in different positions, each chlorine atom in the tetragonal crystal structure of $\text{VOPcCl}_4\text{-p}$ is disordered in two positions with a ratio of 0.514/0.486. $\text{VOPcCl}_4\text{-p}$ molecules in the tetragonal polymorph pack in vertical stacks along the c axis (Figure 4b,c) with the distance between adjacent molecules in a stack of 3.729 Å. The entire $\text{VOPcCl}_4\text{-p}$ molecule appears to be disordered by a mirror plane perpendicular to the tetragonality axis, so it seems that the $\text{VOPcCl}_4\text{-p}$ molecules are oriented “up” and “down” at the same time. This means that individual molecular stacks are randomly oriented either “up” or “down”, and there is no long-range symmetry in their ordering. This style of packing and disordering is not unique and was previously observed in crystals of halogenated lead phthalocyanines $\text{PbPcF}_4\text{-p}$ [38] and $\text{PbPcCl}_4\text{-p}$ [39].

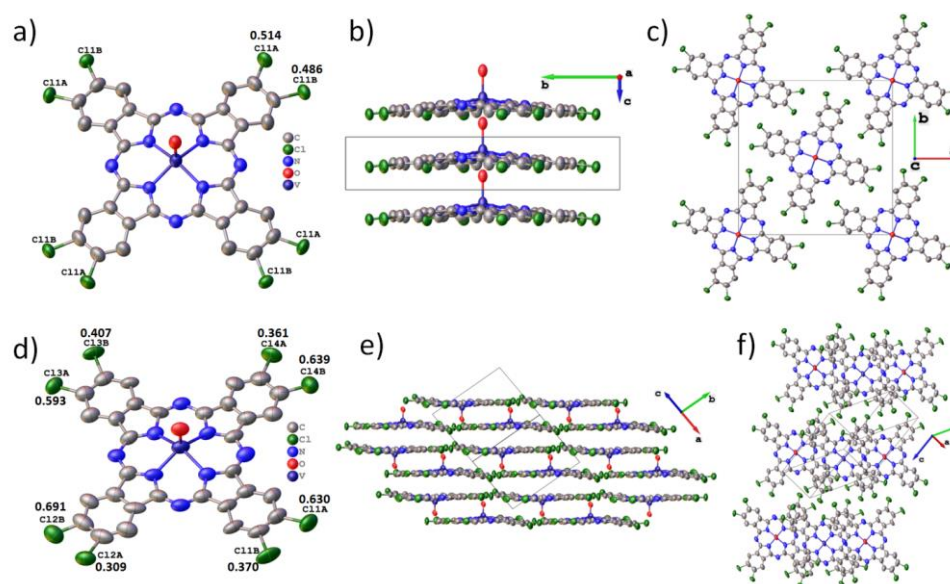


Figure 4. Molecular structure (a) and packing diagrams (b,c) for tetragonal polymorph and molecular structure (d) and packing diagrams (e,f) for triclinic polymorph of VOPcCl₄-p.

Table 1. Unit cell parameters and refinement details for VOPcCl₄ crystal structure.

Compound	VOPcCl ₄ -p (Tetragonal)	VOPcCl ₄ -p (Triclinic)	VOPcCl ₄ -np
Empiric formula	C ₃₂ H ₁₂ Cl ₄ N ₈ OV	C ₃₂ H ₁₂ Cl ₄ N ₈ OV	C ₃₂ H ₁₂ Cl ₄ N ₈ OV
Formula weight	717.24	717.24	717.24
Temperature/K	150	150	150
Crystal system	Tetragonal	Triclinic	Triclinic
Space group	I4/m	P-1	P-1
a/Å	19.5370(10)	9.139(4)	8.9851(16)
b/Å	19.5370(10)	12.716(6)	12.505(2)
c/Å	3.7577(2)	14.291(6)	12.937(2)
α/°	90	114.719(10)	99.740(5)
β/°	90	106.252(11)	96.323(5)
γ/°	90	94.796(11)	95.171(6)
Volume/Å ³	1434.29(17)	1409.5(11)	1415.1(4)
Z	2	2	2
ρ _{calc} g/cm ³	1.661	1.690	1.683
μ/mm ⁻¹	0.764	0.777	0.774
F(000)	718.0	718.0	718.0
Crystal size/mm ³	0.13 × 0.03 × 0.005	0.14 × 0.02 × 0.02	0.03 × 0.03 × 0.01
Radiation	MoK _α (λ = 0.71073)	MoK _α (λ = 0.71073)	MoK _α (λ = 0.71073)
2θ range for data collection/°	4.17 to 51.29	4.78 to 46.874	4.59 to 46.536
Index ranges	−21 ≤ h ≤ 23, −23 ≤ k ≤ 23, −4 ≤ l ≤ 4	−10 ≤ h ≤ 10, −13 ≤ k ≤ 14, −15 ≤ l ≤ 15	−9 ≤ h ≤ 9, −13 ≤ k ≤ 13, −13 ≤ l ≤ 14
Reflections collected	7682	13,062	13,781
Independent reflections	791 [R _{int} = 0.0506, R _{sigma} = 0.0263]	4063 [R _{int} = 0.1507, R _{sigma} = 0.1820]	4054 [R _{int} = 0.1984, R _{sigma} = 0.2193]
Data/restraints/parameters	791/2/107	4063/0/455	4054/12/431
Goodness-of-fit on F ²	1.055	0.968	0.954
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0600, wR ₂ = 0.1659	R ₁ = 0.0881, wR ₂ = 0.2129	R ₁ = 0.0918, wR ₂ = 0.2038
Final R indexes [all data]	R ₁ = 0.0833, wR ₂ = 0.1868	R ₁ = 0.2140, wR ₂ = 0.2839	R ₁ = 0.2459, wR ₂ = 0.2858
Largest diff. peak/hole/e Å ⁻³	0.76/−0.30	0.53/−0.41	1.16/−0.33
CCDC No.	2267526	2267527	2267528

Figure 4d shows a VOPcCl₄-p molecule in triclinic polymorph. While the phthalocyanine core retains the same geometry as in the tetragonal polymorph, there is a clear difference in the distribution of peripheral chlorine atoms in alternative positions. While in the tetragonal polymorph, the distribution is close to 0.5/0.5, in the triclinic polymorph, this ratio is 0.691/0.309, which affects the molecular packaging. In the triclinic polymorph, the VOPcCl₄-p molecules are assembled into chains, with the molecules alternating between an “up” and “down” orientation (Figure 4f). It is worth noting that the sites of chlorine atoms with low occupancy values (<0.5) are those between neighboring molecules in the chain, which means that close Cl...Cl contacts (<2.4 Å) between molecules in the same chain are most likely never present in a real crystal. Thus, the actual closest Cl...Cl contact between molecules in adjacent molecular chains in the triclinic VOPcCl₄-p polymorph is 3.019 Å, which is still significantly shorter than in the tetragonal polymorph (3.364 Å). The distances between adjacent molecules in the chains are 3.217 Å and 3.299 Å. The individual molecular chains are arranged in the form of 2D layers that are packed parallel to the crystallographic plane (−222) (Figure 4e). The distance between molecules in adjacent layers is 3.095 Å, and the angle between the molecular layers and the plane (−222) is ~0.82°.

VOPcCl₄-np crystallizes in the space group P-1 with Z = 2 and Z' = 1 and one symmetrically independent molecule in the unit cell (Table 1). The VOPcCl₄-np molecular structure is shown in Figure 5a. The vanadium atom is displaced from the macrocycle plane by 0.553 Å, and the angle between the V=O bond and the normal to the macrocycle plane is 0.51°. Four chlorine atoms are disordered in two positions each. Their occupancy ratio is similar to the triclinic VOPcCl₄-p polymorph and significantly deviates from the ratio 0.5/0.5.

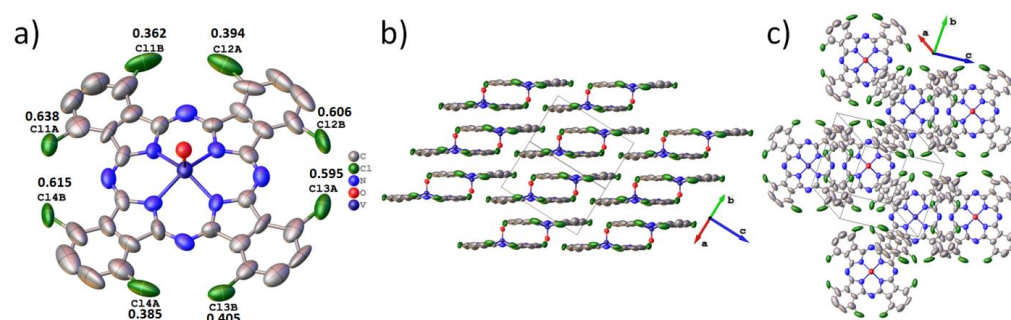


Figure 5. Molecular structure (a) and packing diagrams (b,c) for VOPcCl₄-np.

VOPcCl₄-np molecules are packed into two-dimensional layers parallel to the plane (2−22) (Figure 5b). The distance between molecules in one layer is 3.298 Å, and between adjacent layers, 3.239 Å. The angle between the molecular layers and the plane (2−22) is 0.15°. However, unlike VOPcCl₄-p, VOPcCl₄-np molecules do not form separate chains within one molecular layer but are arranged in such a way that each molecule faces three other molecules (Figure 5c).

3.2. VOPcCl₄-p and VOPcCl₄-np Thin Films and Powder XRD Study

Experimental XRD patterns of VOPcCl₄-p and VOPcCl₄-np powders and thin films (before and after annealing) are shown in Figure 6 in comparison with the powder patterns calculated based on the abovementioned single-crystal data. The first three peaks on the XRD pattern of the VOPcCl₄-p powder (6.38°, 7.19°, and 7.76° 2θ) correspond to the plane (110) of the tetragonal phase and the planes (001) and (010) of the triclinic phase, indicating that both polymorph phases are present in a significant amount in the powder. The strong peak at 27.03° dominates the entire diffraction pattern and belongs to the plane (−222) of the triclinic polymorph, which suggests that the VOPcCl₄-p powder consists mainly of the triclinic phase.

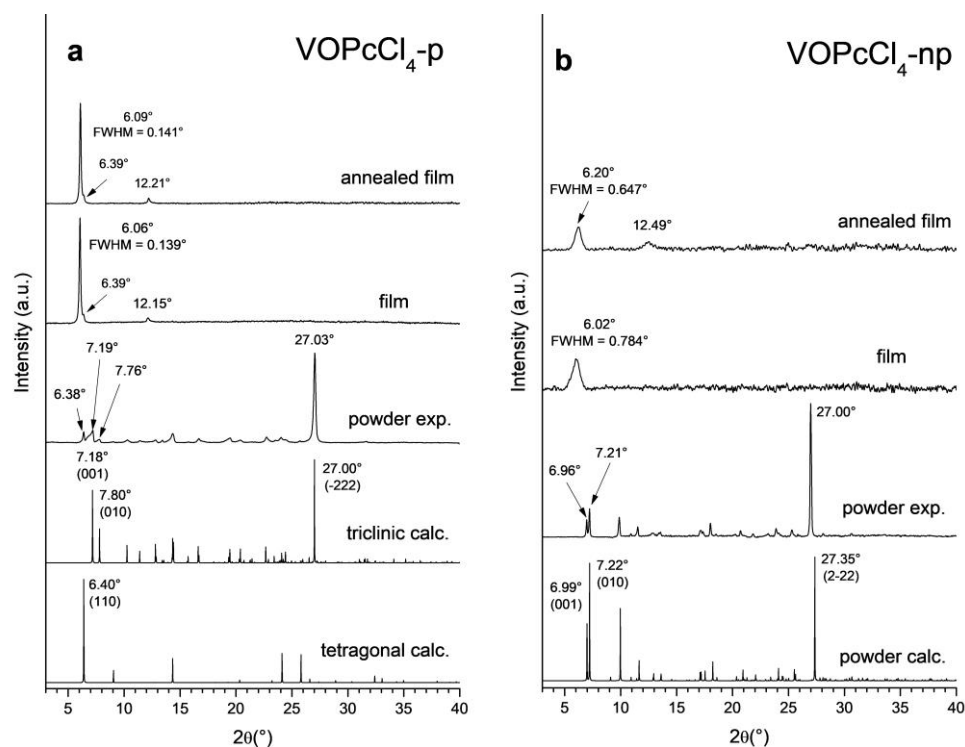


Figure 6. XRD patterns of bulk powders and thin films of VOPcCl₄-p (a) and VOPcCl₄-np (b).

The first two peaks at 6.96° and 7.21° 2θ on the XRD pattern of VOPcCl₄-np powder correspond to the planes (001) and (010), respectively, while the strong peak at 27.00° 2θ corresponds to the plane (2–22). The difference between the calculated and observed position for the peak (2–22) is caused by the difference in sample temperature during the experiment (150 K for SC-XRD and room temperature for PXRD). In general, the experimental powder patterns coincide well with the calculated ones for both VOPcCl₄-p and VOPcCl₄-np.

XRD patterns of both VOPcCl₄-p and VOPcCl₄-np films contain peaks that do not match the single-crystal data. The diffractogram of the VOPcCl₄-p film is characterized by one strong diffraction peak at 6.06° 2θ and a peak at 12.15° 2θ with a weaker intensity, and the diffractogram of the VOPcCl₄-np film contains a diffraction peak at 6.02° 2θ, which belongs to unknown crystal phases. The absence of other strong diffraction peaks indicates that the films have a preferred orientation. The difference in the phase composition of films from single crystals is often observed for phthalocyanines due to the tendency to form different polymorphic modifications depending on temperature [40]. To check the effect of the film annealing on their structure, the films were annealed at 200 °C for 2 h in air. Annealing resulted in a small shift in peak positions toward larger angles but did not change the overall appearance of the diffraction pattern, which can be caused by a release of mechanical stress and a decrease in the number of crystal lattice defects in thin films during annealing.

The optical absorption spectra of VOPcCl₄-p and VOPcCl₄-np films were also recorded. The spectra of VOPcCl₄-p and VOPcCl₄-np films are compared with the spectra of their solutions in dimethylformamide in Supplementary Figure S1. The spectra of VOPcCl₄-p and VOPcCl₄-np solutions are typical for the phthalocyanines, which are present in monomeric form in solutions [41], and have the Q bands with the maxima at 680 and 689 nm, respectively. The spectra of the films become broader because of intermolecular interactions in solids. Similar to the spectra of unsubstituted VOPc [42] and VOPcF₄ [43] films, the maxima of Q bands shift to the higher wavelengths, i.e., to 778 and 795 nm of VOPcCl₄-p and VOPcCl₄-np films, respectively. This view of spectra is a characteristic of

J-aggregate formation [44]. Films' annealing at 200 °C for 2 h does not lead to noticeable changes in the intensity and position of the peaks.

VOPcCl₄-p and VOPcCl₄-np films were also characterized by Raman spectroscopy to demonstrate that their chemical composition coincides with that of the powders. Most of the peak positions in the spectra of the films coincide well with those in the spectra of powders (Supplementary Figure S2). The relative intensities of several peaks are different because of the preferred orientation in thin films, which is especially noticeable in the spectra of VOPcCl₄-p samples.

The morphology of VOPcCl₄-p and VOPcCl₄-np films was studied by AFM. The microscopy images of the films before and after annealing (200 °C, 2 h) are shown in Figure 7.

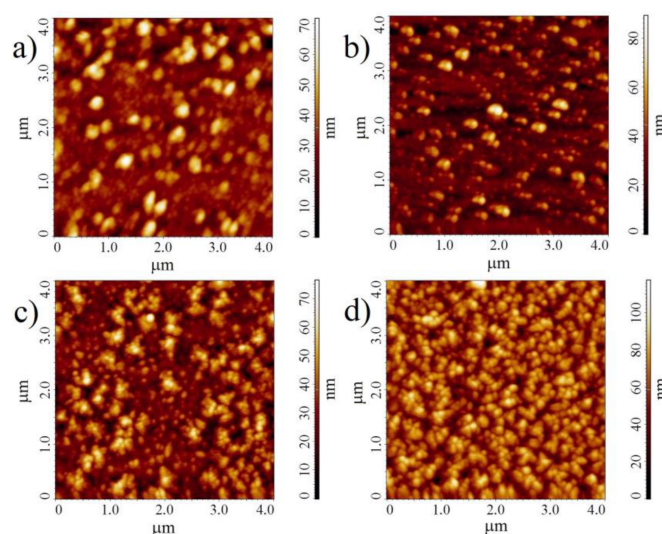


Figure 7. AFM images of VOPcCl₄-p (a) and VOPcCl₄-np (c) before annealing; and VOPcCl₄-p (b) and VOPcCl₄-np (d) after annealing.

The images show that both films are formed by spherical crystallites ranging in size from 50 to 200 nm. The root mean square (RMS) roughness value is 10.4 and 9.9 nm for the VOPcCl₄-p and VOPcCl₄-np films, respectively. After annealing in air, the crystallites increase slightly in size and become more clearly defined and more uniform in size. At the same time, the value of the RMS roughness of the VOPcCl₄-p film decreases to 8.9 nm after annealing, but for VOPcCl₄-np, it increases to 13.0 nm. The films were also characterized by the SEM method (Supplementary Figure S3). The surface of the films in the SEM images looks rough, with indistinctly pronounced rounded grains that become slightly larger after the heat treatment of the films.

3.3. Sensor Properties of VOPcCl₄-p and VOPcCl₄-np Films

3.3.1. Comparison of the Sensor Response of VOPcCl₄-p and VOPcCl₄-np Films to Ammonia

The concentration of NH₃ varied in the range from 1 to 50 ppm. The curves of changes in the sensor response, when different concentrations of NH₃ were introduced, are shown in Figure 8a,b. The measurements of the sensor response were conducted in dynamic mode. In this mode, NH₃ was injected at a constant airflow rate, and its exposure time was 15 s. The resistance of the films of both phthalocyanines increased after the introduction of ammonia into the cell, which was usually observed for metal phthalocyanine films exhibiting p-type semiconductor properties, for example, MPc and MPcF₄ films [31]. The sensor response to NH₃ was completely reversible at room temperature in the investigated concentration range. The dependence of the sensor response of VOPcCl₄-p (a) and VOPcCl₄-np (b) films on NH₃ concentration is shown in Figure 8c. The change in the position of the chlorine substituents in the benzene rings strongly affects the value of the sensor response. For

example, the value of the sensor response of a VOPcCl₄-p film at 10 ppm is 1.6 times higher than that of a VOPcCl₄-np film. A similar trend was previously found for chlorosubstituted zinc phthalocyanines [30]. The dependence of the response on the concentration is linear in the range from 1 to 10 ppm in the case of the VOPcCl₄-p film and from 1 to 5 ppm in the case of the VOPcCl₄-np film, thus making it possible to construct calibration curves in these concentration ranges and to calculate the limit of detection (LOD) according to the formula $3\sigma/m$ (where σ is the standard deviation of the sensor response to 1 ppm of ammonia, while m is the slope of the calibration plot). The calibration curves with the parameters used for the LOD calculation are presented in Supplementary Figure S4. The LODs were estimated to be 0.7 and 0.9 ppm for VOPcCl₄-p and VOPcCl₄-np films, respectively.

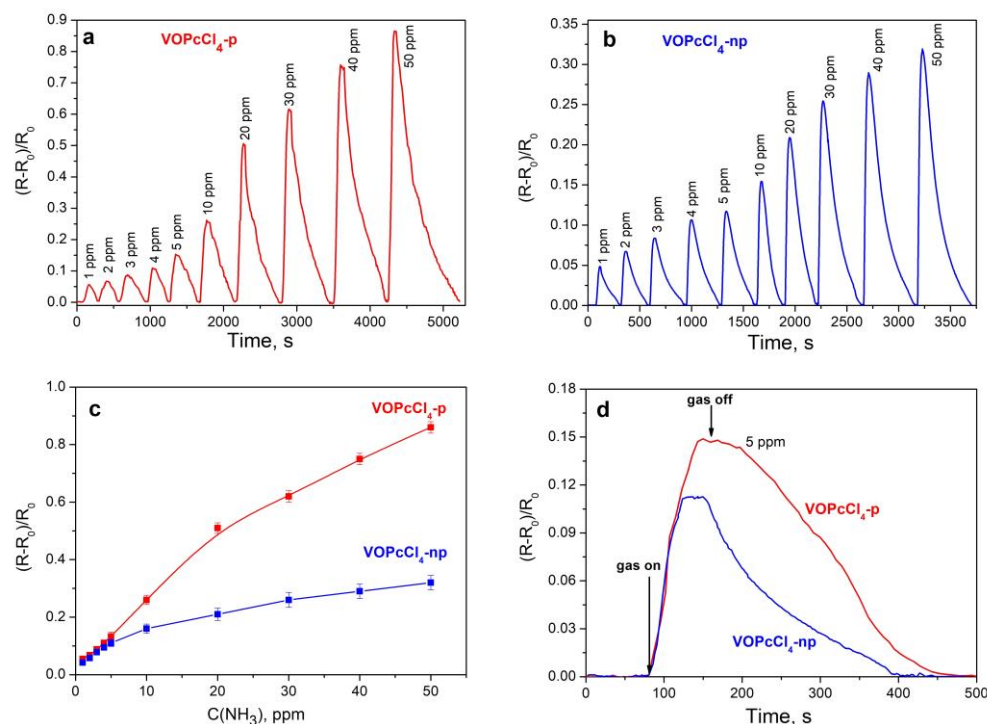


Figure 8. Curves of changes in the sensor response of VOPcCl₄-p (a) and VOPcCl₄-np (b) films when different concentrations of NH₃ (1–50 ppm) are introduced in the flow cell (obtained in dynamic mode). Dependence of the sensor response of VOPcCl₄-p (a) and VOPcCl₄-np (b) films on NH₃ concentration (c). Sensor response of VOPcCl₄-p and VOPcCl₄-np films to 5 ppm of NH₃ (d), measured in the static mode. The measurements were carried out at room temperature (22 ± 2 °C).

To determine the response and recovery times of the sensing layer, the static mode was used. The average response/recovery times measured at 5 ppm NH₃ were 60/300 and 40/270 s for VOPcCl₄-p and VOPcCl₄-np films, respectively. The films of both phthalocyanines demonstrate good repeatability of the sensor response. For example, the value of the sensor response to 1 ppm of NH₃ is 0.055 ± 0.003 when gas is repeatedly injected into the flow cell (Supplementary Figure S5).

3.3.2. Study of the Nature of Interaction between NH₃ and VOPcCl₄ Molecules and Comparison of the Sensor Response of VOPcCl₄ and VOPcF₄ Films

Quantum-chemical calculations of the energy E_b and the nature of NH₃ binding in the corresponding VOPcCl₄-p/NH₃-x and VOPcCl₄-np/NH₃-y aggregates were performed to explain the difference in the sensor response of thin films of chlorosubstituted vanadyl phthalocyanines toward ammonia. In this case, the interaction of a gas molecule with macrocycles through their side atoms was considered (Figures 2 and 3), since it was previously shown that this type of interaction best described the reversible experimental sensor response of the films of phthalocyanines with other substituents and metals [21,23].

It was shown as a result of the calculations that, depending on the position of NH_3 relative to $\text{VOPcCl}_4\text{-p}$, the E_b values vary in the range from 0.171 eV to 0.180 eV (Table 2) and exceed the binding energies in the case of ammonia interaction with $\text{VOPcCl}_4\text{-np}$ (0.149–0.153 eV). The stronger binding between NH_3 molecules and $\text{VOPcCl}_4\text{-p}$ bearing Cl substituents in peripheral positions correlates well with the higher sensor response of a $\text{VOPcCl}_4\text{-p}$ film to ammonia compared to $\text{VOPcCl}_4\text{-np}$. A similar effect was observed earlier for tetrafluorosubstituted phthalocyanines [23].

Table 2. The interaction parameters of the NH_3 molecule with vanadyl phthalocyanines.

Compound	E_b , eV	BCP	Atoms *	$\rho(\mathbf{r})$, $e/\text{\AA}^3$	$\nabla^2\rho(\mathbf{r})$, $e/\text{\AA}^5$
$\text{VOPcCl}_4\text{-p}/\text{NH}_3\text{-1}$	0.174	1	H-N	0.147	1.559
		2	N-H	0.139	1.365
		3	H-N	0.094	1.011
$\text{VOPcCl}_4\text{-p}/\text{NH}_3\text{-2}$	0.180	1	H-N	0.137	1.489
		2	N-H	0.134	1.323
		3	H-N	0.094	1.015
$\text{VOPcCl}_4\text{-p}/\text{NH}_3\text{-3}$	0.180	1	H-N	0.137	1.491
		2	N-H	0.134	1.326
		3	H-N	0.094	1.016
$\text{VOPcCl}_4\text{-p}/\text{NH}_3\text{-4}$	0.171	1	H-N	0.139	1.511
		2	N-H	0.136	1.337
		3	H-N	0.091	0.974
$\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-2}$	0.149	1	H-N	0.105	1.259
		2	N-H	0.102	1.105
		3	Cl-H	0.060	0.789
$\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-3}$	0.153	1	H-N	0.105	1.261
		2	N-H	0.101	1.104
		3	Cl-H	0.060	0.793
$\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-4}$	0.153	1	H-N	0.101	1.090
		2	N-H	0.122	1.228
		3	H-N	0.143	1.566

* The first atom belongs to the phthalocyanine molecule, while the second atom belongs to the NH_3 molecule.

The interaction of ammonia molecules with the side atoms of phthalocyanines occurs due to the formation of hydrogen bonds. This is evidenced by the values of the electron density $\rho(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$ at the corresponding bond critical points (BCPs) (Figures 2 and 3; Table 2). In particular, in the case of $\text{VOPcCl}_4\text{-p}/\text{NH}_3$, hydrogen bonds are formed between the hydrogen atoms of phthalocyanine and the ammonia nitrogen atom (BCP1 and BCP3) and between the bridging nitrogen atom of the macrocycle and one of the hydrogen atoms of the NH_3 molecule (BCP2). The corresponding values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ are in the ranges of 0.091–0.147 $e/\text{\AA}^3$ and 0.974–1.559 $e/\text{\AA}^5$. Similar results were also obtained in the case of aggregates with chlorine atoms in nonperipheral positions of phthalocyanine macroring.

The difference is that in the $\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-2}$ and $\text{VOPcCl}_4\text{-np}/\text{NH}_3\text{-3}$ compounds, one of the hydrogen bonds and the corresponding BCP3 occur between one of the H atoms of NH_3 and the Cl atom. In this case, the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at all considered BCPs are lower and equal to 0.060–0.105 $e/\text{\AA}^3$ and 0.793–1.566 $e/\text{\AA}^5$, respectively. Thus, the stronger NH_3 molecule binding in $\text{VOPcCl}_4\text{-p}/\text{NH}_3$ aggregates compared to $\text{VOPcCl}_4\text{-np}/\text{NH}_3$, in particular, is due to higher electron density values in the corresponding BCPs. The conclusion that ammonia interacts with the side atoms of VOPcCl_4 molecules by forming hydrogen bonds is because the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ are in the ranges of 0.013–0.236 $e/\text{\AA}^3$ and 0.578–3.350 $e/\text{\AA}^5$, respectively (Table 2) [45].

The increase in resistance during the adsorption of NH_3 molecules, which are electron donors, is typical for p-type semiconductors [46], which include thin films of tetrahalo-

gensubstituted phthalocyanines. Therefore, the mechanism of sensor response can be represented using the scheme shown in Figure 9. Ammonia molecules donate electrons to VOPcCl₄ macrocycles due to interaction with their side atoms, thus leading to a decrease in the concentration of holes, i.e., charge carriers, and, consequently, to an increase in the resistance of phthalocyanine films. The stronger the interaction or the higher the gas concentration, the greater the charge transfer and the higher the sensor response.

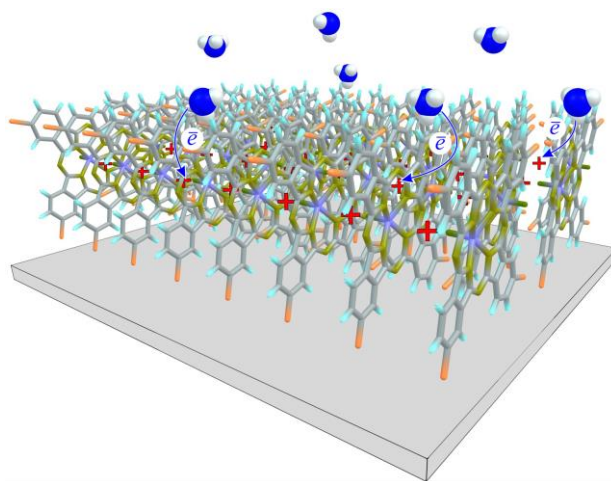


Figure 9. Scheme demonstrating the proposed mechanism of the sensor response. NH₃ molecules donate electrons to macrocycles (blue arrows) due to interaction with their side atoms, leading to a decrease in the concentration of holes (red “plus” signs), i.e., charge carriers, and, consequently, to an increase in the resistance of phthalocyanine films.

It should also be noted that the E_b value of the NH₃ molecule with VOPcCl₄-p is slightly larger than with VOPcF₄-p (0.170–0.174 eV), which was estimated earlier using the same computational approaches. This is consistent with a stronger sensor response of VOPcCl₄ films compared to VOPcF₄ ones. For example, the sensor response $((R - R_0)/R_0)$ of the VOPcCl₄-p film was 0.15 vs. 0.14 (at 5 ppm NH₃) in the case of a VOPcF₄-p film [32]. This difference was even more noticeable at the higher ammonia concentrations (Supplementary Figure S6).

3.3.3. Characteristics of the Sensor Based on VOPcCl₄-p Films

More detailed sensor characteristics were obtained for VOPcCl₄-p films, which possess higher sensitivity to ammonia than VOPcCl₄-np. First, the effect of annealing the films on the value of their sensor response to ammonia was investigated, since it was shown above that the annealing led to a change in the films' morphology (Figure 7). The dynamical curve of the sensor response of the annealed VOPcCl₄-p film is shown in Figure 10a. Figure 10b compares the dependencies of the sensor response of VOPcCl₄-p films before and after annealing on the NH₃ concentration ranging from 1 to 5 ppm. The annealing of VOPcCl₄-p leads to an increase in the sensor response and the slope of the linear dependence of the sensor response on the concentration of NH₃. As a result, the LOD was reduced to 0.3 ppm. The effect may be associated with an increase in the crystallinity of the films. It is known that the conductivity process in polycrystalline films of metal phthalocyanines is greatly influenced by the grain structure and size, as well as intergranular barriers. In several studies, it has been demonstrated that the higher the crystallinity of the film, the grain size, and the packing density of the crystallites, the greater the mobility of the charge carriers [47–49]. The electrical properties of polycrystalline films are determined by the capture of charge carriers in areas localized at the grain boundaries, resulting in a decrease in the free charge carriers involved in conduction and a significant decrease in their mobility due to scattering by potential barriers arising at the boundaries. The larger the average grain sizes in a polycrystalline film, the smaller this barrier. An increase in the charge

carrier mobility in the VOPcCl₄-p film may contribute to a stronger change in the resistance of the film when interacting with NH₃. At the same time, the change in the sensor response of the VOPcCl₄-np film after annealing is less pronounced than in the case of the VOPcCl₄-p film. The recovery time for both vanadyl phthalocyanine films decreased after annealing. The recovery times for annealed VOPcCl₄-p and VOPcCl₄-np films (5 ppm) were 200 and 150 s, respectively.

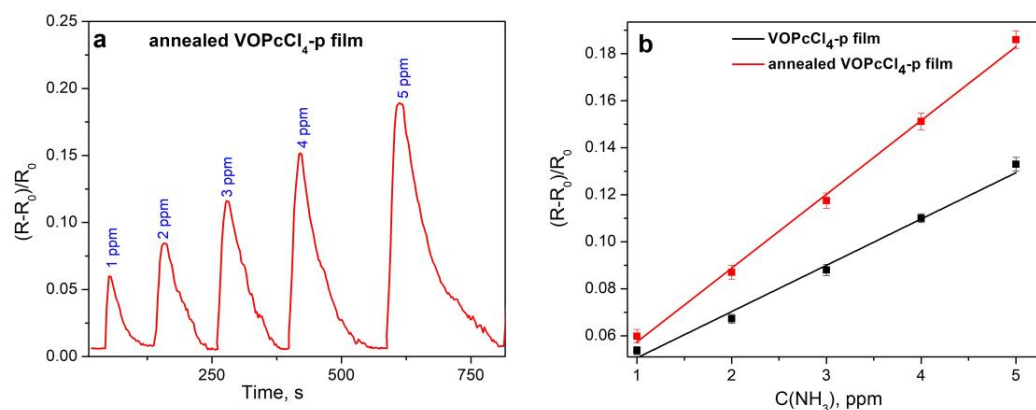


Figure 10. (a) Dynamical curve of the sensor response of the annealed VOPcCl₄-p film to ammonia (1–5 ppm). (b) Sensor response of VOPcCl₄-p film to ammonia (1–5 ppm) before (black line) and after (red line) annealing in air (200 °C, 2 h). The measurements were carried out at room temperature (22 ± 2 °C).

The sensor response of as-deposited and annealed VOPcCl₄-p films to ammonia (1–5 ppm) was tested at different levels of relative humidity (RH) (Figure 11a,c). With an increase in RH from 5 to 40%, the sensor response of both VOPcCl₄-p films practically does not change; however, a further increase in RH to 60% leads to the growth of the sensor response by about 1.6 times. Similar to ammonia, the water molecule is also an electron donor; therefore, the simultaneous exposure of the film by the mixture of NH₃ and H₂O leads to an increase in its sensor response.

As already noted in the introduction, an increased level of ammonia in the exhaled air may be a sign of renal pathologies. The study of exhaled air for elevated levels of ammonia can be a convenient tool for the primary diagnosis of kidney diseases. To test the possibility of using phthalocyanine films in exhaled air, the measurements of their sensor response to some other gases (NO, CO₂, and hydrogen) and volatile organic compounds (VOCs) that may be present in exhaled air, as well as to NH₃ in a mixture of gases similar in composition to exhaled air, were carried out. The diagrams exhibiting the sensor response of as-deposited and annealed VOPcCl₄-p films to these analytes in comparison with ammonia are shown in Figure 11b,d. Similarly to fluorosubstituted metal phthalocyanines [31], the VOPcCl₄-p films exhibit a significantly higher response to NH₃ than to the investigated VOCs and other gases, except for nitric oxide (Figure 11b,d). Note that the concentration of these gases is much higher than that of ammonia. In this case, NO is an interfering gas, and the detection of ammonia may be difficult, even if it is present in the gas mixture at the ppb level. This is especially important to take into account when studying biomarker gases in exhaled air. For example, in a healthy person, the NO concentration can be found in the concentration range of 10–50 ppb, while the ammonia concentration can rise from 0.5 ppm in a healthy person to around 2 ppm in the case of liver or kidney failure [50]. Therefore, the effect of the presence of nitric oxide on the sensor response to ammonia is the subject of further investigation.

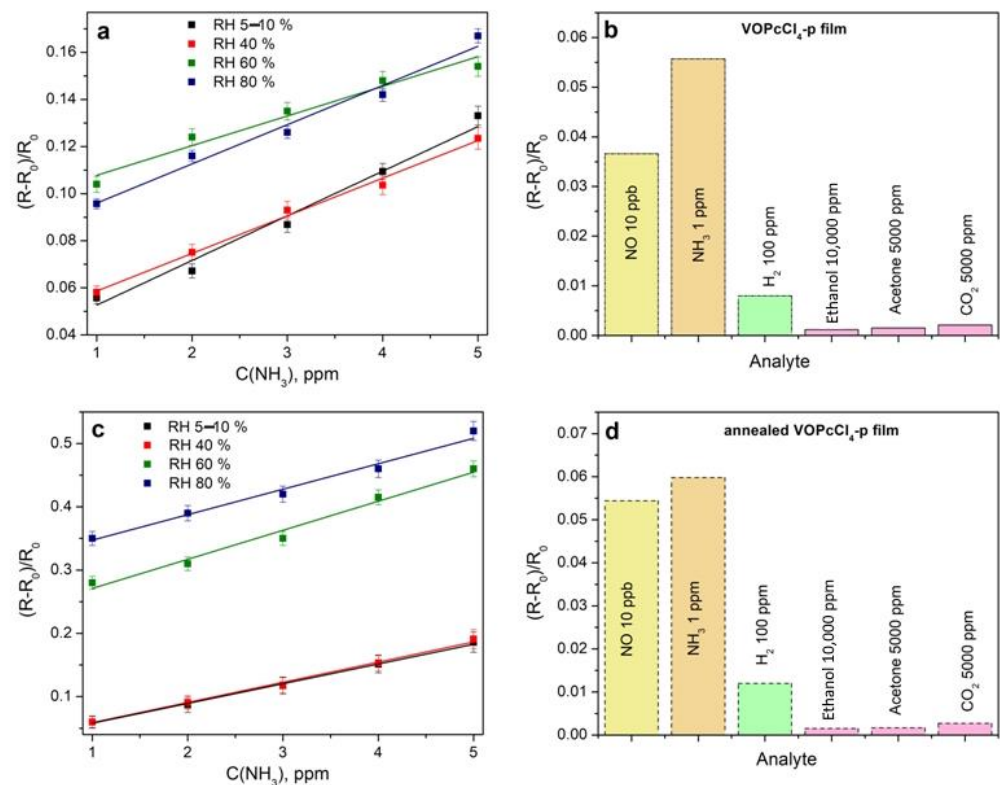


Figure 11. Sensor response of as-deposited and annealed VOPcCl₄-p films to ammonia (1–5 ppm) at different levels of relative humidity (a,c) and to various gaseous analytes and volatile organic vapors (b,d). The measurements were carried out at room temperature ($22 \pm 2^\circ\text{C}$).

Figure 12 shows the sensor response of an annealed VOPcCl₄-p film to ammonia (1–4 ppm) in a mixture of gases simulating exhaled air in comparison with that measured in moist air. This mixture contained N₂ (76%), O₂ (16%), H₂O (5%), and CO₂ (3%). It should be noted that the relative humidity of the moist air and the gas mixture was the same and was maintained at 80–85%. It can be seen from Figure 11 that the sensor response to ammonia in this mixture is almost the same as in moist air. Thus, films based on chlorinated vanadyl phthalocyanines can potentially be used to detect the low ammonia concentration in human-exhaled air. Tests of real exhaled samples are beyond the scope of this work, as they require the involvement of other methods to study their composition.

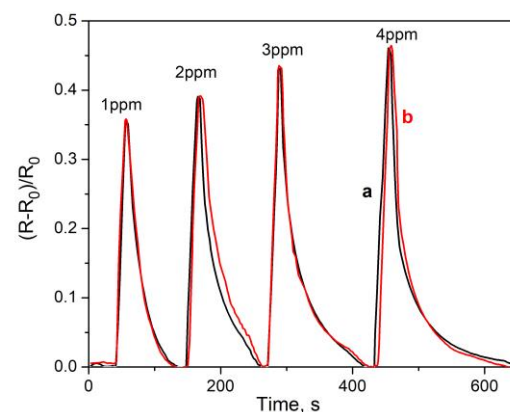


Figure 12. The sensor response of a VOPcCl₄-p film to ammonia (1–4 ppm) in moist air (a) and in a mixture of gases similar in composition to exhaled air (b). RH of the moist air and the gas mixture was the same and was maintained at 80–85%. The measurements were carried out at room temperature ($22 \pm 2^\circ\text{C}$).

To test the long-term stability of the sensor, the response of the annealed VOPcCl₄-p films was measured after 1, 2, 7, and 30 days (see Supplementary Figure S7). It was shown that the films demonstrate good stability, and the change in their sensor response after a fairly long time was within the experimental error.

The sensor characteristics of as-deposited and annealed VOPcCl₄-p films were compared with other sensors based on metal phthalocyanines and relative compounds studied in recent works (Table 3). It can be seen that both the as-deposited and annealed VOPcCl₄-p films can compete with sensors based on films of other metal phthalocyanines, and the sensitivity of the annealed films even exceeds the value of the sensor response of the films presented in Table 3. Only halogenated cobalt and zinc phthalocyanine films studied in our previous works [30,32,51] had a lower detection limit than the VOPcCl₄-p films, but the recovery time of the VOPcCl₄-p films is lower (150 s) and the value of the sensor response (52%) is higher compared to that of the CoPcF₄-p films (215 s and 41%, respectively) and ZnPcF₄-p (210 s and 16%, respectively). Thus, this study makes it possible to expand the range of metal phthalocyanines, which are promising materials for use as active layers of chemiresistive sensors to ammonia.

Table 3. Sensor characteristics of as-deposited and annealed VOPcCl₄-p films in comparison with other sensors based on metal phthalocyanines and relative compounds.

Layers	Sensor Response, % *	LOD, ppb	Linear Range, ppm	Response Time, s	Recovery Time, s	Refs.
VOPcF ₄ -p	14 (5 ppm)	40	1–10	48 (at 5 ppm)	270 (at 5 ppm)	[32]
CoPcF ₄ -p	41 (5 ppm)	10	1–10	55	215	[32]
ClAlPc	11.5 (1 ppm)	100	0.1–1	60 (fixed)	n/a	[52]
Cl ₂ SiPc/LuPc ₂	13 (10 ppm)	100	10–90	<60 (at 90 ppm)	<420 (at 90 ppm)	[53]
TiOTPP **	25 ± 2 (1 ppm)	50	0–0.75	90	1200	[54]
Tetrakis(n-octylthio) phthalocyaninato copper(II)	~20 (10 ppm)	n/a	10–50	50 (at 30 ppm)	30 (at 30 ppm)	[55]
p-isopropylbenzene/LuPc ₂	~20 (10 ppm)	n/a	10–90	60 (fixed)	240 (fixed)	[56]
CoPcR ₈ ***	2.8 (5 ppm)	30	0.3–50	20 (at 5 ppm)	40 (at 5 ppm)	[51]
ZnPcF ₄ -p	16 (5 ppm)	10	0.1–50	45 (at 1 ppm)	210 (at 1 ppm)	[30]
ZnPcCl ₄ -p	18 (5 ppm)	10	0.1–50	45 (1 ppm)	260 (1 ppm)	
VOPcCl ₄ -p	15 (5 ppm)	70	1–10	60 (at 5 ppm)	200 (at 5 ppm)	This work
Annealed VOPcCl ₄ -p	52 (5 ppm)	30	1–10	50 (at 5 ppm)	150 (at 5 ppm)	This work

* The sensor response is defined as $(R - R_0)/R_0 \cdot 100\%$ and provided for those concentrations that are indicated in the corresponding reference; ** TPP is tetraphenylporphyrin; *** R is 5-(trifluoromethyl)-2-mercaptopyridine.

Our analysis of review articles devoted to the study of ammonia sensors showed that resistive sensors based on semiconductor oxides and their hybrid materials have a lower response (4–30 s) and relaxation times (10–90 s) compared to sensors based on fluorosubstituted phthalocyanines; however, their detection limits are usually worse and vary (i.e., 0.1–20 ppm) [57,58]. Sensors of ammonia based on OFET structures [57] with conductive polymers as sensing layers have low LODs (usually from tens to hundreds parts per billion) that are comparable with phthalocyanine films, but usually their response and recovery times are quite high and range from several minutes to tens of minutes.

As a rule, the active layers of sensors with better characteristics than those of phthalocyanine films are not single-component films but mixtures of complex organic semiconductors [59,60] or complex heterostructures, for example, oxides or conductive polymers modified with nanoparticles or carbon nanomaterials [61,62]. Compared with such heterostructures, the advantage of phthalocyanine films lies in the simplicity of the production method.

4. Conclusions

In this work, the films of tetrachlorosubstituted vanadyl phthalocyanine derivatives were studied as active layers for detecting low concentrations of NH_3 . Tetrachlorosubstituted vanadyl phthalocyanines with Cl substituents in the peripheral (VOPcCl₄-p) and nonperipheral (VOPcCl₄-np) positions of the phthalocyanine ring were investigated to reveal the effect of the position of substituents on the structure of their films prepared by a physical vapor deposition technique and their sensor response to ammonia. It was shown that the films of VOPcCl₄-p exhibited a noticeably higher sensor response to both NH_3 films when compared to VOPcCl₄-np films. This was explained with the help of quantum chemical calculations by the stronger interaction of NH_3 molecules with the side atoms of phthalocyanine having peripheral Cl substituents as compared to the phthalocyanines bearing the substituents in the nonperipheral position of the macrocycle. The limit of detection (LOD) of NH_3 was 0.7 ppm. The postdeposition annealing of the films allowed us to increase the sensor response and reduce the detection limit to 0.3 ppm. The sensing layers demonstrated a reversible sensor response at room temperature, with fairly low response/recovery times of 50/300 s at 5 ppm NH_3 . The fact that NH_3 can be detected in the presence of various interfering gases and vapors, as well as in a mixture of gases similar in composition to exhaled air, indicates that VOPcCl₄ films may be good candidates for their use as active layers for detecting ammonia as a biomarker in exhaled air. However, a lot of effort is still needed to improve their selectivity, as well as the response time, which is higher than that of most sensors based on semiconductor oxides. Therefore, further efforts should be directed to testing phthalocyanine-based sensing layers and their arrays in multicomponent gas mixtures and to study hybrid materials of metal phthalocyanines with metal nanoparticles and/or carbon nanomaterials, which are known to contribute to improving sensor performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/mi14091773/s1>, Figure S1. Optical absorption spectra of the solutions of VOPcCl₄-p and VOPcCl₄-np in dimethylformamide (black lines) and their films before (blue lines) and after (red lines) heat treatment; Figure S2. Raman spectra of VOPcCl₄-p and VOPcCl₄-np films (blue lines) and powders (black lines); Figure S3. SEM images of VOPcCl₄-p and VOPcCl₄-np (black lines) and their films before (a,c) and after (b,d) heat treatment; Figure S4. Dependencies of the sensor response and fitting parameters used for the calculation of LODs of VOPcCl₄-p and VOPcCl₄-np films; Figure S5. Repeatability of the sensor response of a VOPcCl₄-p film, measured at 1 ppm of NH_3 ; Figure S6. Comparison of the dependence of the sensor response on ammonia concentration for VOPcCl₄-p and VOPcF₄-p films; Figure S7. The sensor response of an annealed VOPcCl₄-p film to 1 ppm of NH_3 , measured in 1, 2, 7, and 30 days.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author. VOPcCl₄-p and VOPcCl₄-np structural data can be obtained from

<https://www.ccdc.cam.ac.uk/structures/>, accessed on 13 September 2023 (numbers 2267526, 2267527, and 2267528).

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References

- Choudhari, U.; Jagtap, S. A panoramic view of NO_x and NH₃ gas sensors. *Nano-Struct. Nano-Objects* **2023**, *35*, 100995. [CrossRef]
- Close, L.G.; Catlin, F.I.; Cohn, A.M. Acute and chronic effects of ammonia burns of the respiratory tract. *Arch. Otolaryngol.* **1980**, *106*, 151–158. [CrossRef] [PubMed]
- Timmer, B.; Olthuis, W.; Van Den Berg, A. Ammonia sensors and their applications—A review. *Sens. Actuators B Chem.* **2005**, *107*, 666–677. [CrossRef]
- Freddi, S.; Marzuoli, C.; Pagliara, S.; Drera, G.; Sangaletti, L. Targeting biomarkers in the gas phase through a chemoresistive electronic nose based on graphene functionalized with metal phthalocyanines. *RSC Adv.* **2022**, *13*, 251–263. [CrossRef]
- Liu, L.; Fei, T.; Guan, X.; Zhao, H.; Zhang, T. Humidity-activated ammonia sensor with excellent selectivity for exhaled breath analysis. *Sens. Actuators B Chem.* **2021**, *334*, 129625. [CrossRef]
- Lefferts, M.J.; Castell, M.R. Ammonia breath analysis. *Sens. Diagn.* **2022**, *1*, 955–967. [CrossRef]
- Kim, S.; Moon, J.; Kwak, H.J.; Kim, S.I.; Park, D.W.; Kim, J.W.; Kim, T.H.; Sohn, J.W.; Shin, D.H.; Park, S.S.; et al. Comparison of two exhaled nitric oxide analyzers: The NIOX MINO hand-held electrochemical analyzer and the NOA280i stationary chemiluminescence analyzer. *Respirology* **2012**, *17*, 830–834. [CrossRef]
- Pan, S.; Tian, Y.; Li, M.; Zhao, J.; Zhu, L.; Zhang, W.; Gu, H.; Wang, H.; Shi, J.; Fang, X.; et al. Quantitative detection of nitric oxide in exhaled human breath by extractive electrospray ionization mass spectrometry. *Sci. Rep.* **2015**, *5*, 8725. [CrossRef]
- Budde, W.L. Ron hites: Gas chromatography/mass spectrometry pioneer and the Great detector debate. *Environ. Sci. Technol.* **2015**, *49*, 13741–13742. [CrossRef]
- Dey, A. Semiconductor metal oxide gas sensors: A review. *Mater. Sci. Eng. B* **2018**, *229*, 206–217. [CrossRef]
- Uma, S.; Shobana, M.K. Metal oxide semiconductor gas sensors in clinical diagnosis and environmental monitoring. *Sens. Actuators A Phys.* **2023**, *349*, 114044. [CrossRef]
- Qin, R.; Shan, G.; Hu, M.; Huang, W. Two-dimensional transition metal carbides and/or nitrides (MXenes) and their applications in sensors. *Mater. Today Phys.* **2021**, *21*, 100527. [CrossRef]
- Li, J.; Chen, X.; Zhu, X.; Jiang, Y.; Chang, X.; Sun, S. Two-dimensional transition metal MXene-based gas sensors: A review. *Chin. Chem. Lett.* **2023**, 108286. [CrossRef]
- Xiao, Z.; Kong, L.B.; Ruan, S.; Li, X.; Yu, S.; Li, X.; Jiang, Y.; Yao, Z.; Ye, S.; Wang, C.; et al. Recent development in nanocarbon materials for gas sensor applications. *Sens. Actuators B Chem.* **2018**, *274*, 235–267. [CrossRef]
- Rana, M.K.; Sinha, M.; Panda, S. Gas sensing behavior of metal-phthalocyanines: Effects of electronic structure on sensitivity. *Chem. Phys.* **2018**, *513*, 23–34. [CrossRef]
- Şahin, Z.; Meunier-Prest, R.; Dumoulin, F.; Kumar, A.; İsci, Ü.; Bouvet, M. Tuning of organic heterojunction conductivity by the substituents' electronic effects in phthalocyanines for ambipolar gas sensors. *Sens. Actuators B Chem.* **2021**, *332*, 129505. [CrossRef]
- Saini, R.; Kaur, R.; Devi, P.; Gasso, S.; Sharma, S. Tailoring the performance of phthalocyanine-based sensor: Side chain substitution and nanofabrication. *Mater. Today Proc.* **2023**. [CrossRef]
- Singh, A.; Kumar, A.; Kumar, A.; Samanta, S.; Joshi, N.; Balouria, V.; Debnath, A.K.; Prasad, R.; Salmi, Z.; Chehimi, M.M.; et al. Bending stress induced improved chemiresistive gas sensing characteristics of flexible cobalt-phthalocyanine thin films. *Appl. Phys. Lett.* **2013**, *102*, 132107. [CrossRef]
- Gounden, D.; Nombona, N.; van Zyl, W.E. Recent advances in phthalocyanines for chemical sensor, non-linear optics (NLO) and energy storage applications. *Coord. Chem. Rev.* **2020**, *420*, 213359. [CrossRef]
- Liu, C.J.; Peng, C.H.; Ju, Y.H.; Hsieh, J.C. Titanyl phthalocyanine gas sensor for NO₂ detection. *Sens. Actuators B Chem.* **1998**, *52*, 264–269. [CrossRef]
- Elesh, E.; Mohammed, Z. Morphological, linear and nonlinear properties of gallium phthalocyanine chloride annealed thin films. *Optik* **2020**, *219*, 165176. [CrossRef]
- Ziolo, R.F.; Griffiths, C.H.; Troup, J.M. Crystal structure of vanadyl phthalocyanine, phase II. *J. Chem. Soc. Dalt. Trans.* **1980**, 575, 2300–2302. [CrossRef]
- Handa, M.; Suzuki, A.; Shoji, S.; Kasuga, K.; Sogabe, K. Spectral and electrochemical properties of vanadyl hexadecafluorophthalocyanine. *Inorganica Chim. Acta* **1995**, *230*, 41–44. [CrossRef]
- Wang, H.; Song, D.; Yang, J.; Yu, B.; Geng, Y.; Yan, D. High mobility vanadyl-phthalocyanine polycrystalline films for organic field-effect transistors. *Appl. Phys. Lett.* **2007**, *90*, 253510. [CrossRef]
- Wang, X.; Ji, S.; Wang, H.; Yan, D. Room temperature nitrogen dioxide chemresistor using ultrathin vanadyl-phthalocyanine film as active layer. *Sens. Actuators B Chem.* **2011**, *160*, 115–120. [CrossRef]

26. Aziz, F.; Sayyad, M.H.; Karimov, K.S.; Saleem, M.; Ahmad, Z.; Khan, S.M. Characterization of vanadyl phthalocyanine based surface-type capacitive humidity sensors. *J. Semicond.* **2010**, *31*, 114002. [\[CrossRef\]](#)
27. Roslan, N.A.; Abu Bakar, A.; Bawazeer, T.M.; Alsoufi, M.S.; Alsenany, N.; Abdul Majid, W.H.; Supangat, A. Enhancing the performance of vanadyl phthalocyanine-based humidity sensor by varying the thickness. *Sens. Actuators B Chem.* **2019**, *279*, 148–156. [\[CrossRef\]](#)
28. Ji, S.; Wang, H.; Wang, T.; Yan, D. A high-performance room-temperature NO₂ sensor based on an ultrathin heterojunction film. *Adv. Mater.* **2013**, *25*, 1755–1760. [\[CrossRef\]](#)
29. Schöllhorn, B.; Germain, J.P.; Pauly, A.; Maleysson, C.; Blanc, J.P. Influence of peripheral electron-withdrawing substituents on the conductivity of zinc phthalocyanine in the presence of gases. Part 1: Reducing gases. *Thin Solid Film.* **1998**, *326*, 245–250. [\[CrossRef\]](#)
30. Bonegardt, D.; Klyamer, D.; Sukhikh, A.; Krasnov, P.; Popovetskiy, P.; Basova, T. Fluorination vs. Chlorination: Effect on the Sensor Response of Tetrasubstituted Zinc Phthalocyanine Films to Ammonia. *Chemosensors* **2021**, *9*, 137. [\[CrossRef\]](#)
31. Klyamer, D.; Sukhikh, A.; Nikolaeva, N.; Morozova, N.; Basova, T. Vanadyl phthalocyanine films and their hybrid structures with Pd nanoparticles: Structure and sensing properties. *Sensors* **2020**, *20*, 1893. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Klyamer, D.; Bonegardt, D.; Krasnov, P.; Sukhikh, A.; Popovetskiy, P.; Basova, T. Tetrafluorosubstituted Metal Phthalocyanines: Study of the Effect of the Position of Fluorine Substituents on the Chemiresistive Sensor Response to Ammonia. *Chemosensors* **2022**, *10*, 515. [\[CrossRef\]](#)
33. Klyamer, D.D.; Sukhikh, A.S.; Gromilov, S.A.; Kruchinin, V.N.; Spesivtsev, E.V.; Hassan, A.K.; Basova, T.V. Influence of fluorosubstitution on the structure of zinc phthalocyanine thin films. *Macrocycles* **2018**, *11*, 304–311. [\[CrossRef\]](#)
34. APEX3, v.2019.1-0; Bruker AXS Inc.: Madison, WI, USA, 2019.
35. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [\[CrossRef\]](#)
36. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [\[CrossRef\]](#)
38. Kuprikova, N.M.; Klyamer, D.D.; Sukhikh, A.S.; Krasnov, P.O.; Mrsic, I.; Basova, T.V. Fluorosubstituted lead phthalocyanines: Crystal structure, spectral and sensing properties. *Dye. Pigment.* **2020**, *173*, 107939. [\[CrossRef\]](#)
39. Klyamer, D.D.; Sukhikh, A.S.; Bonegardt, D.V.; Basova, T.V. Tetrachlorosubstituted Lead Phthalocyanines: Effect of the Positions of Substituents on the Structure of Single Crystals and thin Films. *J. Struct. Chem.* **2023**, *64*, 650–661. [\[CrossRef\]](#)
40. Wang, H.; Zhou, Y.; Roy, V.A.L.; Yan, D.; Zhang, J.; Lee, C.S. Polymorphism and electronic properties of vanadyl-phthalocyanine films. *Org. Electron.* **2014**, *15*, 1586–1591. [\[CrossRef\]](#)
41. van Faassen, E.E.; Schlettwein, D. Energy Migratoin and Light-Induced Charge Transfer at Phthalocyanine Surfaces. In *Handbook of Photochemistry and Photobiology, Vol. 3: Supramolecular Photochemistry*; Nalwa, H.S., Ed.; American Scientific: Valencia, CA, USA, 2003; pp. 355–409.
42. Yamashita, A.; Maruno, T.; Hayashi, T. Absorption spectra of organic-molecular-beam-deposited vanadyl- and titanylphthalocyanine. *J. Phys. Chem.* **2002**, *97*, 4567–4569. [\[CrossRef\]](#)
43. Sukhikh, A.; Bonegardt, D.; Klyamer, D.; Basova, T. Effect of non-peripheral fluorosubstitution on the structure of metal phthalocyanines and their films. *Dye. Pigment.* **2021**, *192*, 109442. [\[CrossRef\]](#)
44. Zhang, X.F.; Xi, Q.; Zhao, J. Fluorescent and triplet state photoactive J-type phthalocyanine nano assemblies: Controlled formation and photosensitizing properties. *J. Mater. Chem.* **2010**, *20*, 6726–6733. [\[CrossRef\]](#)
45. Bushmarinov, I.S.; Lyssenko, K.A.; Antipin, M.Y. Atomic energy in the “Atoms in Molecules” theory and its use for solving chemical problems. *Russ. Chem. Rev.* **2009**, *78*, 283–302. [\[CrossRef\]](#)
46. Wisitsoraat, A.; Tuantranont, A.; Comini, E.; Sberveglieri, G.; Wlodarski, W. Characterization of n-type and p-type semiconductor gas sensors based on NiOx doped TiO₂ thin films. *Thin Solid Film.* **2009**, *517*, 2775–2780. [\[CrossRef\]](#)
47. Li, Y.; Pan, M.; Hu, Y.; Wang, Z.; Lv, W.; Peng, Y. The influence of substrate temperature on the near-infrared absorption and carrier mobility of lead phthalocyanine phototransistors. *Thin Solid Film.* **2021**, *718*, 138481. [\[CrossRef\]](#)
48. Nénon, S.; Kanehira, D.; Yoshimoto, N.; Fages, F.; Vidélot-Ackermann, C. Shelf-life time test of p- and n-channel organic thin film transistors using copper phthalocyanines. *Thin Solid Film.* **2010**, *518*, 5593–5598. [\[CrossRef\]](#)
49. Wu, F.C.; Cheng, H.L.; Yen, C.H.; Lin, J.W.; Liu, S.J.; Chou, W.Y.; Tang, F.C. Electron transport properties in fluorinated copper-phthalocyanine films: Importance of vibrational reorganization energy and molecular microstructure. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2098–2106. [\[CrossRef\]](#)
50. Das, S.; Pal, M. Non-Invasive Monitoring of Human Health by Exhaled Breath Analysis: A Comprehensive Review. *J. Electrochem. Soc.* **2020**, *167*, 037562. [\[CrossRef\]](#)
51. Kaya, E.N.; Şenocak, A.; Klyamer, D.D.; Demirbaş, E.; Basova, T.V.; Durmuş, M. Ammonia sensing performance of thin films of cobalt(II) phthalocyanine bearing fluorinated substituents. *J. Mater. Sci. Mater. Electron.* **2019**, *8*, 7543–7551. [\[CrossRef\]](#)
52. Madhaiyan, G.; Sun, A.T.; Zan, H.W.; Meng, H.F.; Horng, S.F.; Chen, L.Y.; Hung, H.W. Solution-processed chloroaluminum phthalocyanine (Clalpc) ammonia gas sensor with vertical organic porous diodes. *Sensors* **2021**, *21*, 5783. [\[CrossRef\]](#)

53. Ganesh Moorthy, S.; King, B.; Kumar, A.; Lesniewska, E.; Lessard, B.H.; Bouvet, M. Molecular Engineering of Silicon Phthalocyanine to Improve the Charge Transport and Ammonia Sensing Properties of Organic Heterojunction Gas Sensors. *Adv. Sens. Res.* **2023**, *2*, 2200030. [[CrossRef](#)]
54. Trul, A.A.; Chekusova, V.P.; Polinskaya, M.S.; Kiselev, A.N.; Agina, E.V.; Ponomarenko, S.A. NH₃ and H₂S real-time detection in the humid air by two-layer Langmuir-Schaefer OFETs. *Sens. Actuators B Chem.* **2020**, *321*, 128609. [[CrossRef](#)]
55. Gülmez, A.D.; Polyakov, M.S.; Volchek, V.V.; Kostakoğlu, S.T.; Esenpinar, A.A.; Basova, T.V.; Durmuş, M.; Gürek, A.G.; Ahsen, V.; Banimuslem, H.A.; et al. Tetrasubstituted copper phthalocyanines: Correlation between liquid crystalline properties, films alignment and sensing properties. *Sens. Actuators B Chem.* **2017**, *241*, 364–375. [[CrossRef](#)]
56. Kumar, A.; Meunier-Prest, R.; Herbst, F.; Heintz, O.; Lesniewska, E.; Bouvet, M. Covalent grafting of aryls to modulate the electrical properties of phthalocyanine-based heterostructures: Application to ammonia sensing. *Chem. Eng. J.* **2022**, *436*, 135207. [[CrossRef](#)]
57. Kwak, D.; Lei, Y.; Maric, R. Ammonia gas sensors: A comprehensive review. *Talanta* **2019**, *204*, 713–730. [[CrossRef](#)]
58. Aarya, S.; Kumar, Y.; Chahota, R.K. Recent Advances in Materials, Parameters, Performance and Technology in Ammonia Sensors: A Review. *J. Inorg. Organomet. Polym. Mater.* **2020**, *30*, 269–290. [[CrossRef](#)]
59. Zhang, F.J.; Di, C.A.; Berdunov, N.; Hu, Y.; Hu, Y.; Gao, X.; Meng, Q.; Sirringhaus, H.; Zhu, D. Ultrathin film organic transistors: Precise control of semiconductor thickness via spin-coating. *Adv. Mater.* **2013**, *25*, 1401–1407. [[CrossRef](#)]
60. Zhang, F.; Qu, G.; Mohammadi, E.; Mei, J.; Diao, Y. Solution-Processed Nanoporous Organic Semiconductor Thin Films: Toward Health and Environmental Monitoring of Volatile Markers. *Adv. Funct. Mater.* **2017**, *27*, 1701117. [[CrossRef](#)]
61. Li, L.; Gao, P.; Baumgarten, M.; Müllen, K.; Lu, N.; Fuchs, H.; Chi, L. High performance field-effect ammonia sensors based on a structured ultrathin organic semiconductor film. *Adv. Mater.* **2013**, *25*, 3419–3425. [[CrossRef](#)]
62. Zhang, S.; Zhao, Y.; Du, X.; Chu, Y.; Zhang, S.; Huang, J. Gas Sensors Based on Nano/Microstructured Organic Field-Effect Transistors. *Small* **2019**, *15*, 1805196. [[CrossRef](#)]

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