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Electronic and gas sensing properties of soluble phthalocyanines[*]

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Some optical and electrical properties of 3-diethylamino-1-propylsulfonamide substituted zinc and metal-free phthalocyanines are presented. These materials are sensitive to NO_2 even at concentrations as low as 0.1–2.5 ppm. Electrical conductivity and photoconductivity were used as the detection methods.

Key words: *substituted phthalocyanine; nitrogen dioxide sensor; optical properties; photoconductivity*

1. Introduction

Phthalocyanines (Pcs) are organic molecules consisting of a planar π-conjugated skeleton with a metal or two hydrogen atoms at the centre. They are solid under usual conditions, stable (up to 400 °C) organic semiconductors, used in many electronic and photonic applications, like photodetectors, gas sensors, transistors, solar cells, non-linear optical media, etc. [1]. Pcs are coloured, absorbing light mainly in two regions, 250–350 nm (Soret band) and 600–700 nm (Q-band) [2-4]; therefore, visible light can be used for photoelectronic applications [5]. Phthalocyanines have already been proposed as active layers for NO_2 detection. The majority of authors studied copper phthalocyanine sensitivity under various conditions. Cadmium, cobalt, aluminium [6, 7], plumbum [8] and lanthanide phthalocyanines [9] were also studied as NO_2 sensors. There is little information available about the use of Zn and metal-free Pcs for NO_2 sensor application.

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Very often the method of vacuum evaporation is used for Pc thin film preparation. For non-soluble Pcs, vacuum evaporation seems to be one of the simplest methods for the deposition of homogeneous thin films of controlled thicknesses. This method has some shortcomings, among others the high cost for industrial applications. When exposed to NO_2, the conductivity of such vacuum evaporated thin films increases. It is hard to compare absolute values of the increase, as presented by various authors, because of different deposition conditions, temperature, etc. Generally, according to the literature, responses are slow and not easily reproducible. The reverse part of the kinetic process is very often longer than 3 h [10, 11]. The increase in temperature improves the reversibility. Usually temperatures between 150 and 200 °C are necessary. However, this limits the application possibilities of the sensor.

Several approaches such as use of modified sample substrates have been applied to improve the sensor reaction speed and recovery, as well as to simplify the deposition conditions. The use of porous silicon with pores filled with Pc reduces the recovery time to 10 min [6], while the sensitivity to NO_2 remains the same. Another approach is to use substituted Pc as a sensing layer. These Pcs are often soluble, which makes it possible to use cold wet technologies for layer deposition, like spin coating, dipping, drop-casting and ink-jet printing. Although electronic properties of non-soluble phthalocyanines have been very well established, only limited information about substituted soluble derivatives is available. In this paper, we present some optical, photoelectrical and gas sensing properties of two soluble phthalocyanines, viz. 3-diethylamino-1-propylsulphonamide-Zn-phthalocyanine (ZnPcSu) and its metal-free (H_2PcSu) analogue. Sulfonamide substituent acts as a relatively strong electron acceptor; thus, a semiconductor of n-type is available [12]. Optical and electrical gas detection is discussed in the paper. In this paper, the terms “optical gas detection” and “electrical gas detection” mean the change of optical properties and electrical properties of the material under the influence of the studied gas, respectively.

2. Experimental

2.1. Materials

Two 3-diethylamino-1-propylsulphonamide substituted phthalocyanines were studied in this work: one with a Zn atom and the other with two hydrogen atoms at the centre of the Pc skeleton.

Synthesis of metal-free phthalocyanine (H_2Pc). Metal free phthalocyanine was prepared according to the US Pat. 3.297712. 300 g of 1,2-dicyanobenzene was suspended in 270 g of quinoline and subsequently heated under a hydrogen blanket in an autoclave (volume 2000 cm^3, pressure 10 MPa, temperature 200 °C) for 8 h. After the reaction had been completed, the dark blue suspension was taken out from the autoclave and filtered.

The filtered cake was thoroughly washed with acetone and dried until a constant weight had been achieved. This way, 106,4 g of dark blue product was obtained.

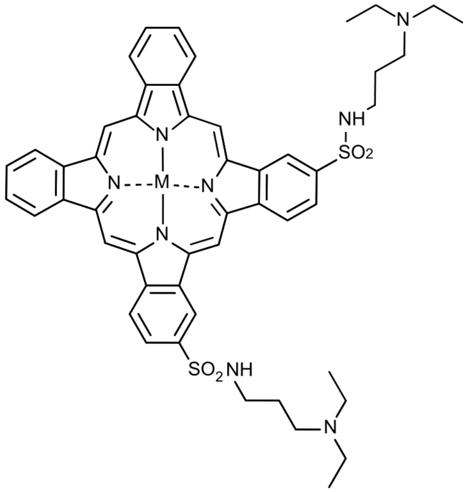
Synthesis of metal-free phthalocyanine sulfochloride. 10 g of H_2Pc was dissolved in 56 g of chlorosulfonic acid and heated in a 500 cm^3 Keller flask, equipped with an agitator, thermometer, dropping funnel and reflux cooler, at the temperature of 100 °C for 30 min. The reaction mixture was cooled down to a temperature of 85 °C by agitating and subsequently 14.5 g of thionyl chloride was gradually added with a dropping funnel into the reaction mixture at the temperature between 80 and 85 °C. When thionyl chloride was charged, the reaction mixture was heated for 2 h at 100 °C. The reaction mixture was cooled down by agitating to the laboratory temperature and gradually added into the agitated mixture of 1000 g ice and 1500 cm^3 water. Precipitated H_2Pc sulfochloride was filtered and washed with ice-water until the analytical test with $BaCl_2$ solution on sulfate anion was negative. 62 g of wet H_2Pc sulfochloride filter cake was obtained. Small sample, ca. 10 g of the wet filter cake, was dispersed in methanol, filtered, washed with methanol, filtered and dried. The hydrolysable chlorine content was determined by argentometric titration, after alkaline hydrolysis of the dry sample. The content of hydrolysable chlorine was found to be 11.2%. The average number of SO_2Cl groups on each H_2Pc molecule was 2.2. The rest of wet filter cake was kept in a freezer box at –18 °C.

Synthesis of metal-free phthalocyanine sulfonamide (H_2PcSu). 52 g of the frozen filter cake of H_2Pc sulfochloride was crushed and fully dispersed by agitation in 26 cm^3 of water. The temperature of the mixture was 3 °C. After H_2Pc sulfochloride had been fully dispersed, 10 g of N,N-diethyl-1,3-propanediamine was added into the dispersion at once. The temperature of the mixture immediately reached 16 °C. The mixture was then subsequently agitated at 60 °C for 6 h. The reaction mixture was then filtered and the filter cake of sulfonamide was thoroughly washed with water and dried until a constant weight of 4.5 g of dry product had been obtained.

Synthesis of zinc phthalocyanine (ZnPc). 43 g 1,2-dicyanobenzene, 15.6 g anhydrous zinc chloride, 45 cm^3 ethanol and 25 cm^3 ethanolic solution of sodium ethanolate (0.01 g of Na per cm^3) were placed in a 500 cm^3 flask equipped with an agitator, thermometer, dropping funnel and a cooler. The mixture was agitated and heated in order to remove ethanol by distillation. Ethanol was gradually changed for 1-octanol, which was gradually added into the mixture through a dropping funnel. The reaction mixture was agitated at 175 °C for 3 h. Then the mixture was cooled down to 110 °C, the distillation cooler was changed for the reflux cooler and 250 cm^3 of ethanol was added into the reaction mixture through the dropping funnel. The dark blue product was isolated by filtration, thoroughly washed with ethanol, water and dried to a constant weight. 36.4 g of zinc phthalocyanine was obtained this way. Its purity was 95.5 %, as estimated from the quantity of Zn, which was found to be 10.8 %.

Synthesis of zinc phthalocyanine sulfochloride. 20 g of ZnPc was dissolved in 112 g of chlorosulfonic acid and heated in 500 cm^3 Keller flask, equipped with an agitator, thermometer, dropping funnel and reflux cooler, at 100 °C for 30 min. The reaction mixture was cooled by agitation to 85 °C and subsequently 20 g of thionyl chloride was gradually added through a dropping funnel into the reaction mixture at the temperature between 80 °C and 85 °C. After all the thionyl chloride had been used, the reaction mixture was heated for 2 h at 100 °C. The reaction mixture was then cooled by agitation to room temperature and gradually added into the agitated mixture of 1000 g ice and 1500 cm^3 water. The precipitated ZnPc sulfochloride was filtered and washed with ice-water until the analytical test with $BaCl_2$ solution on sulfate anion was negative. 80 g of wet ZnPc sulfochloride filter cake was obtained. A small sample, ca. 10 g of wet filter cake, was dispersed in methanol, filtered, washed with methanol, filtered and dried. The hydrolysable chlorine content was determined by the argentometric titration, after alkaline hydrolysis of the dry sample. The content of hydrolysable chlorine was found to be 8.1 %. The average number of SO_2Cl groups on each ZnPc molecule was 1.5. The rest of the wet filter cake was kept in a freezer box at –18 °C.

Synthesis of zinc phthalocyanine sulfonamide (ZnPcSu). 70 g of frozen filter cake of ZnPc sulfochloride was crushed and fully dispersed by agitation in 40 cm^3 of water. The temperature of the mixture was 3 °C. After the ZnPc sulfochloride had fully dispersed, 20 g of N,N-diethyl-1,3-propanediamine was charged into the dispersion at once. The temperature of the mixture immediately reached 28 °C. The mixture was then subsequently agitated at 60 °C for 6 h. The reaction mixture was then filtered and the filter cake of sulfonamide was thoroughly washed with water. The washed filter cake was dried until a constant weight had been achieved. 16 g of dry product was obtained. The chemical structures of Pcs under study are shown in Scheme 1.



Scheme 1. Structural formula of phthalocyanines under study. M = 2H or Zn

2.2. Samples

Samples with various structures were used in the experiments. UV-grade fused silica glass substrates were used for optical transmittance measurements. Samples for optical gas detection in transmittance mode were prepared using UV-grade fused silica spectroscopic cuvettes (Fig. 1).

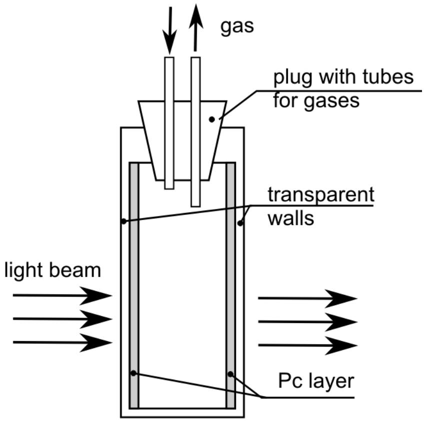


Fig. 1. Modified cuvette with Pc layer
for optical gas sensitivity measurements

Thin films of Pcs were deposited on the inner sides of the cuvette from the solution by drop-casting. After drying, the cuvette was closed with a modified plug containing thin tubes for gas supply and gas extraction. The atmosphere inside the cuvette was controlled by the gas flowing through these tubes. The design of the cuvette allowed the measurements of optical spectra during the exposure of the samples to the analyte gas. For the electrical and photoelectrical measurements, ceramic substrates with interdigital gold electrodes were used. Pcs were deposited over the electrodes. The distance between electrodes was 30 μm. A schematic diagram of the substrates used in this study is shown in Fig. 2.

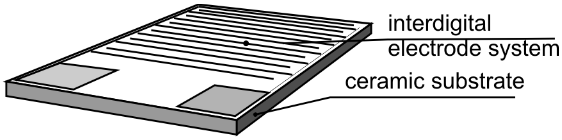


Fig. 2. Substrate with interdigital electrode system
for electrical and gas sensitivity measurements

Substrates made of fused silica glasses were washed in hot peroxysulfuric acid for 15 min, then rinsed thoroughly with distilled water and dried. Ceramic substrates were cleaned in isopropanol vapours for 10 min and then dried. Thin films were deposited by the spin-coating technique and by drop-casting from chloroform solution onto freshly cleaned substrates. The films were homogeneous; their thicknesses were approximately 20–30 nm. The thicknesses of the films were measured using a Taylor –Hobson Talystep profilometer .

2.3. Measurements

Optical absorption spectra were measured using a Perkin-Elmer Lambda 950 UV -VIS-NIR spectrometer. IR spectra were recorded with a Perkin-Elmer Paragon 1000PC FTIR spectrometer using a single-bounce, attenuated total reflection method.

Electrical measurements were performed in a dc regime, using a Keithley 6517A electrometer. Red light emitting diode (λ = 670 nm) or quartz tungsten halogen lamp equipped with a Corner Stone monochromator from Lot Oriel Gruppe Europa were used for the sample illumination in photoconductivity studies.

The electrical response to gas exposure was tested in a 62.8 cm^3 sample chamber, made of stainless steel (Fig. 3). Gas exposure was realized using a continuous flow of a carrier gas mixed with the analyte in a predefined proportion and at a constant flow rate. Atmospheric air was used as a carrier gas, a 100 ppm mixture of NO_2 with synthetic air was used as the analyte gas. The presence of oxygen in the mixture prevents the transformation of NO_2 to other nitrogen oxides N_xO_y.

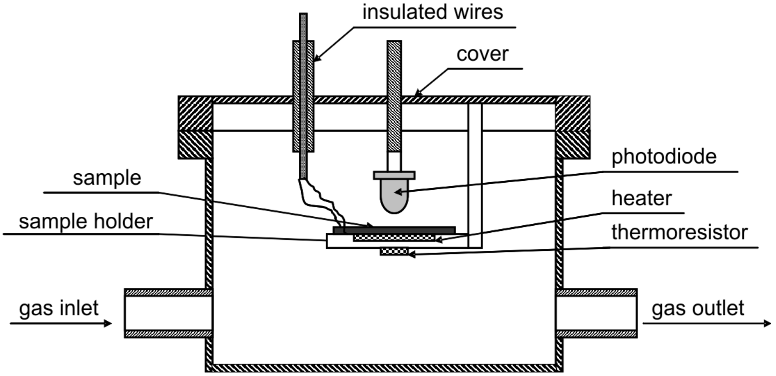


Fig. 3. Scheme of the chamber for gas sensing measurements

The amount of the gas passing through the sample chamber as well as the content of NO_2 were controlled by two gas mass flow controllers. Carrier gas flow was controlled using an Alicat Scientific MC 16 series flow controller, while the analyte gas flow was regulated by an Omega FMA3703 flow controller. Carrier and analyte gases were mixed and supplied to the sample chamber. All electrical gas sensing measurements were performed according to the following scenario: First, the chamber was purged with a pure carrier gas until the electrical current was stabilized. Then, the inflow of the mixture of a given concentration of NO_2 was applied for 50 min. After that the sample was exposed to pure carrier gas for 50 min. The procedure was repeated for several NO_2 concentrations.

3. Results and discussion

3.1. Optical properties

Absorption spectra of ZnPcSu thin films (Fig. 4) are characterized by two main bands: the Soret or B-band with a maximum at 338 nm, and the Q-band with a maximum at 680 nm. The former band is related to d–π* electronic transition, the latter one to π–π* electronic transition of the phthalocyanine skeleton [13]. The spectrum of H_2PcSu thin film is also shown in Fig. 4 (curve 2). The character of the spectrum is similar to that of ZnPcSu. The Soret and Q-bands show maxima at 334 and 626 nm, respectively. Energy gaps E_g were determined from the low-energy onset of Q-band absorption in the $(h\nu\alpha)^2$ vs. $h\nu$ plot (α is the absorption coefficient, h is the Planck constant and ν is the wavenumber). For both Pcs, $E_g = 1.7$ eV. It is worth noting that the absorption coefficient of H_2PcSu is higher than that of ZnPcSu.

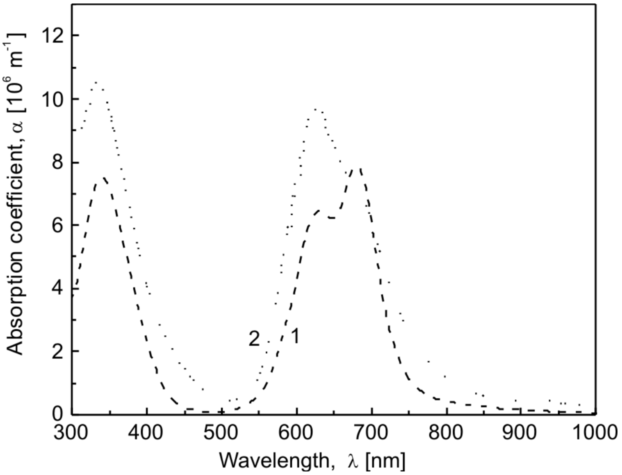


Fig. 4. Absorption spectra of ZnPcSu (curve 1) and H_2PcSu (curve 2) thin films

Infrared spectra of studied materials are shown in Fig. 5. The peaks at 3284 cm^{-1} and 1016 cm^{-1} (curve 2) can be assigned to central N–H stretching and bending vibrations, respectively. These bands are missing in the ZnPcSu spectrum (curve 1), which corresponds to the structural difference between ZnPcSu and H_2PcSu. All other peaks characteristic of non-substituted phthalocyanines [14, 15] are present in the spectra. There are unassigned peaks present in both spectra: 475(sh), 487(w), 500(w), 516(w), 552(m), 564(m), 576(sh), 611(w), 651(w), 661(sh), 720(vs), 807(m), 836(w), 849(w), 923(vw), 951(m), 1046(s), 1075(sh), 1137(s), 1185(m), 1254(s), 1387(s), 1451(s), 1653(w), 1714(w), 2549(m), 2806(m), 2965 cm^{-1}(s).

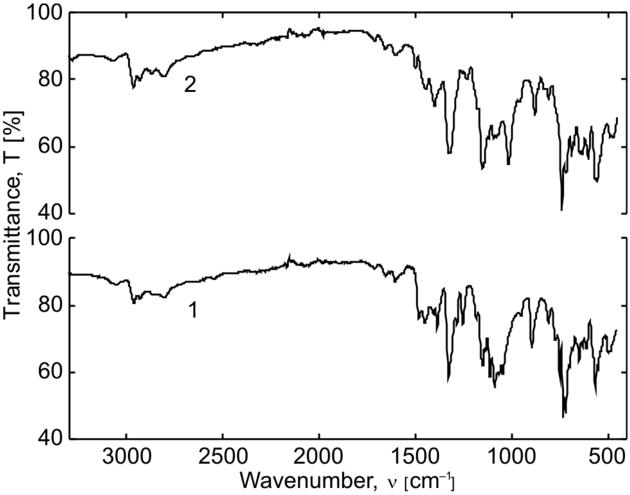


Fig. 5. Infrared spectra of ZnPcSu (curve 1) and H_2PcSu (curve 2)

3.2. Optical gas detection

We have found minor changes in the absorption spectrum of ZnPcSu during NO_2 exposure. The changes are presented in Fig. 6 in the form of the differential transmittance spectrum.

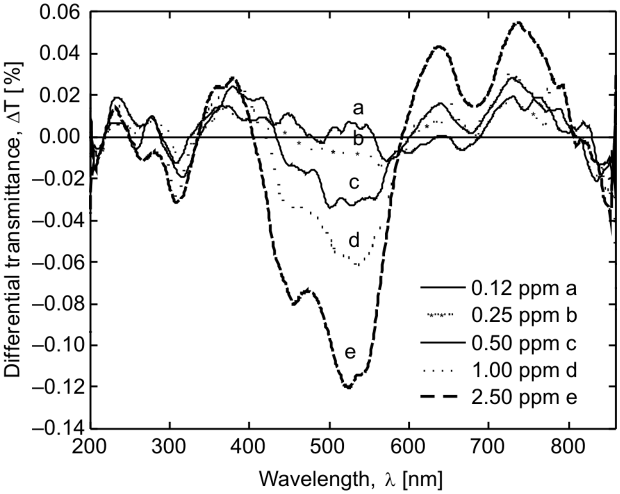


Fig. 6. Differential transmittance spectra of ZnPcSu thin film
in the presence of NO_2; concentrations from 0.12 ppm to 2.50 ppm.
The reference is the spectrum of neat ZnPcSu

The positive values in the picture correspond to increases in the transmittance, whereas negative values correspond to decreases in the transmittance upon exposure to NO_2. The main changes are: the decrease in the absorption in the Q-band region, and the increase in the absorption around 500 nm. This increase of the absorption can be associated with an exciplex band. Some changes were also observed around 233, 307 and 380 nm, which is consistent with the reports of other authors [9, 16, 17].

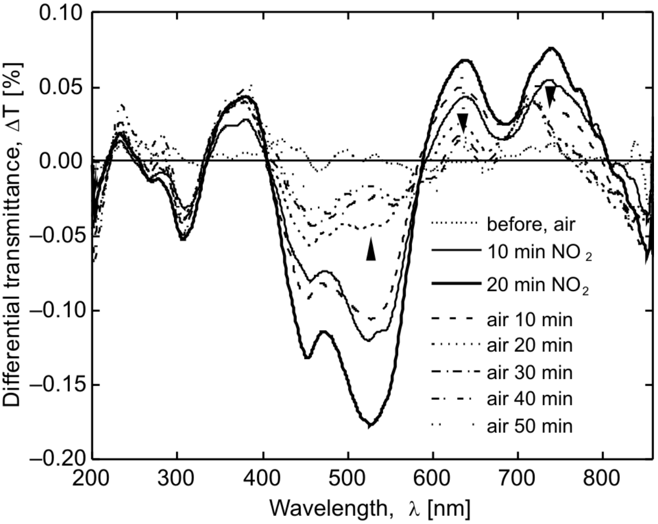


Fig. 7. Differential transmittance spectra of ZnPcSu after the NO_2 exposure (concentration 2.50 ppm, 10 and 20 min) and their relaxation on air

In order to investigate the reversibility of the changes described above, the cuvette previously filled with NO_2 mixture was purged with clean carrier gas for 1 h. During this time, the absorption spectra were measured at 10 min intervals (Fig. 7). It was found that the band in the region 400–600 nm almost disappeared after 1 h of purging (reversibility 92 %). The value of the Q-band differential transmittance also decreased, but the reversibility at 637 nm was only 85%.

There was no change in the absorption spectra of H_2PcSu under the NO_2 exposure.

3.3. Electrical properties

Dark current–voltage characteristics were ohmic for both the studied Pcs. The dark current of the ZnPcSu sample was 4 orders of magnitude lower than that of the H_2PcSu sample. The activation energy of the dark current, measured in the temperature range 15–80 °C, was 0.77 eV for both the phthalocyanines under study. These values are close to the halves of the energy gaps determined optically (see above), which suggests that there is practically no dopant present in the material.

Under illumination with monochromatic light at the maximum of photocurrent in the region of Q-band (λ = 596 nm for H_2PcSu and 598 nm for ZnPcSu, see Fig. 8), a strong current increase was observed; three orders of magnitude for ZnPcSu and 1.5 order of magnitude for H_2PcSu (photon flux $\varphi = 0.76$ W/m^2). The spectrum of the photoelectrical response roughly followed the absorption spectrum (Fig. 8). The shift of the photoresponse maximum to the blue region, in the comparison with the absorption spectrum, could be caused by long-time processes (the spectra were recorded in the red to blue region).

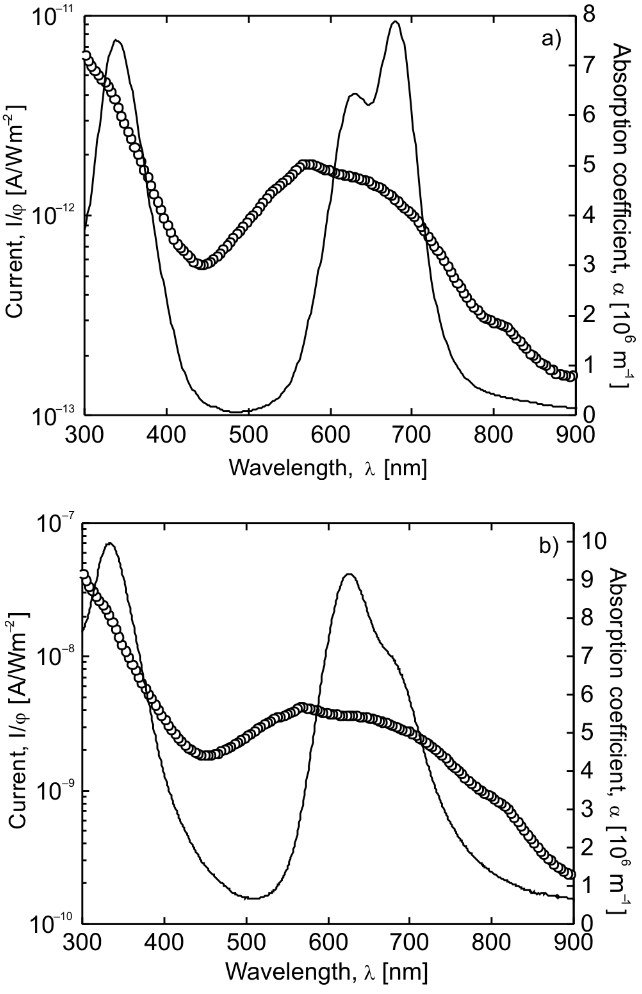


Fig. 8. Photoresponses and absorption spectra of thin films of phthalocyanines under study: a) spectra of ZnPcSu, b) spectra of H_2PcSu

The photocurrent kinetics showed a stable behaviour in the dark and under illumination (Fig. 9). Immediately after the sample illumination a quite fast current increase was observed. However, the steady state conditions were not reached even after 30 min. After switching off the light, the current returned to the dark value after ca. 30 min for ZnPcSu and after a few hours for H_2PcSu.

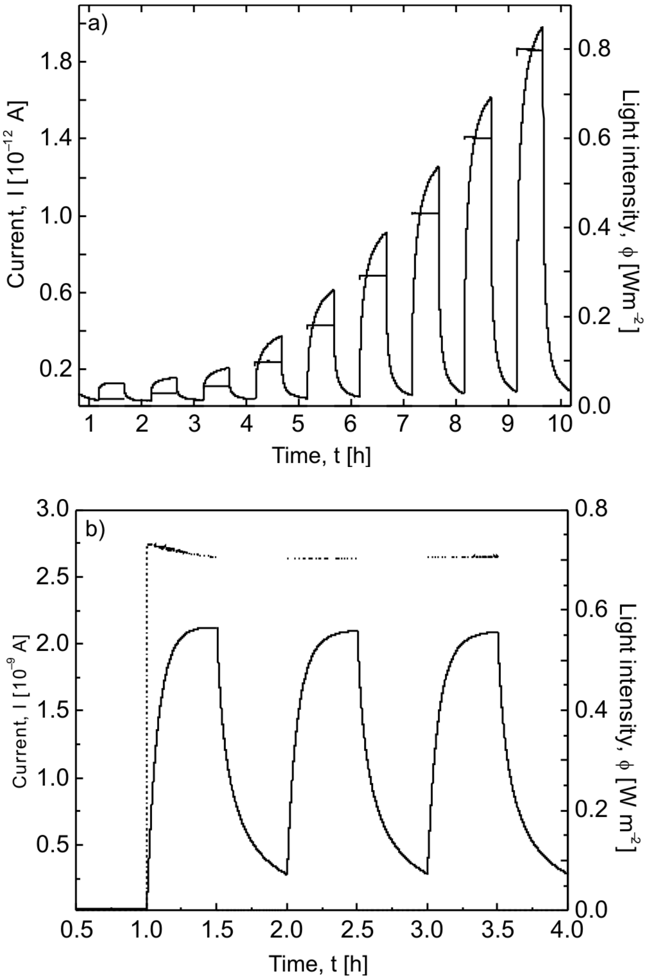


Fig. 9. Photocurrent kinetic of studied phthalocyanines: a) – ZnPcSu, b) – H_2PcSu.
Light intensity scenario is plotted with thin curves, photoelectric response in thick ones

This behaviour seems to be unusual because the electrical conductivity of H_2PcSu is four orders of magnitude higher than that of ZnPcSu. One reason for this behaviour could be the formation of deep traps. This supposition is supported by the shape of the dependence of current I on the light intensity ϕ, which is of the type $I = \phi^n$, $n = 0.8$. This suggests the influence of traps on charge carrier transport. However, the shapes of long time kinetics do not show behaviour consistent with the space charge formation, i.e., the current decrease after the current saturation (see Fig. 9b). This behaviour, which is not important from the point of view of sensor design, needs additional study.

3.4. Electrical gas detection

Electrical sensitivity of ZnPcSu to NO_2 exposure is shown in Fig. 10. Electrical response could be detected even for concentrations of several hundred ppb at room temperature. At the concentration of 2.50 ppm, the dark current increase was already two orders of magnitude. The response consisted of a fast and a slow part. The signal did not reach saturation even after 40 min. However, the duration of the fast response could be estimated to be about 5 min. The characteristic time of the slow reverse process was much longer still. It explains the gradual increase of the current at the end of clean carrier gas exposure following each step of NO_2 exposure (shift of baseline). Under the NO_2 exposure, the photocurrent response shows behaviour similar to that of the dark current under the NO_2 exposure. However, the photocurrent sensitivity was significantly lower (see Fig. 10, curve 2).

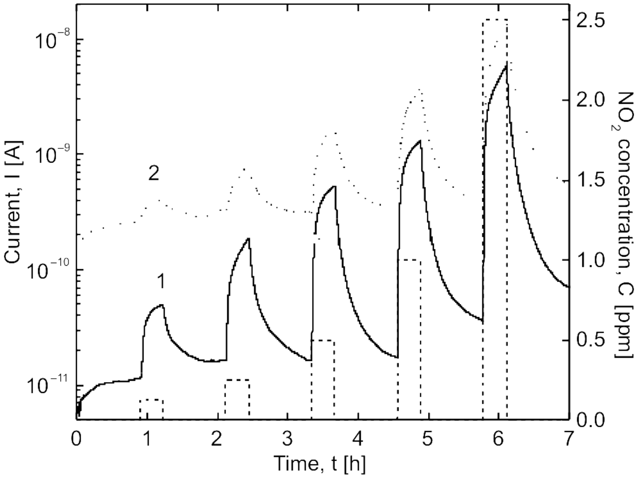


Fig. 10. Kinetics of the current of ZnPcSu thin film during NO_2 exposure of various concentrations: 1 – dark current, line 2 – photocurrent. The dashed line shows the scenario of the NO_2 exposure and concentration

A qualitatively different behaviour was found for H_2PcSu, investigated under the same conditions as ZnPcSu. Kinetic curves are shown in Fig. 11. The basic differences were: both dark and photocurrent response under the NO_2 exposure were opposite, ie. the current decreased upon exposure to the gas. The dark current change was much smaller. The dark current responses were smaller at higher NO_2 concentrations. Conversely – with the sample under illumination, the photocurrent response during the NO_2 exposure was fast, the slow component was missing, and the response was fully reversible. Photocurrent stabilization was achieved in about 15 min under the exposure to NO_2, the reverse process was complete after about 15–20 min.

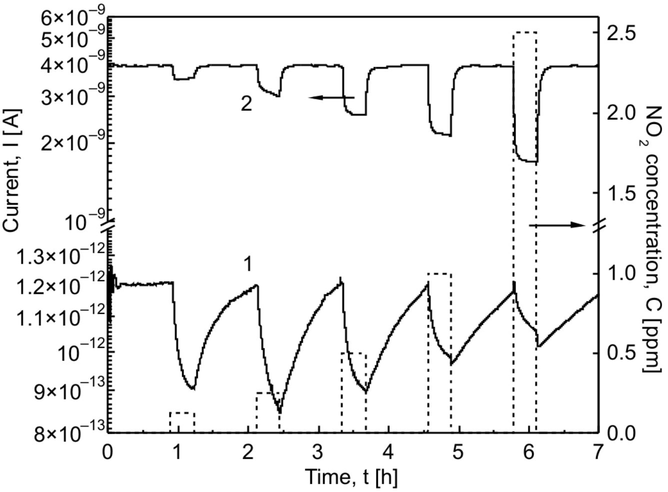


Fig. 11. Kinetics of the current change of H_2PcSu thin film during NO_2 exposure of various concentrations: 1 – dark current change, 2 – photocurrent change. The dashed lines show the history of the NO_2 exposure and its concentration

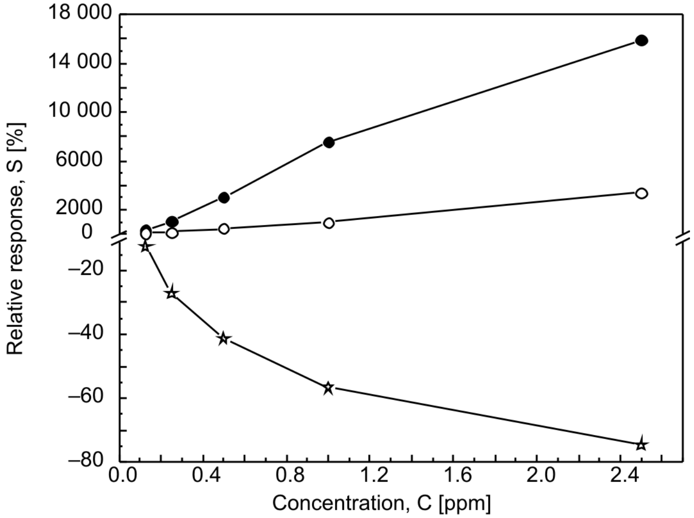


Fig. 12. Electrical sensitivity of ZnPcSu to NO_2 in the dark (filled dots), under illumination (empty dots), and of H_2PcSu to NO_2 under illumination (stars)

The comparison of the above described sensitivities to NO_2 for both investigated materials is shown in Fig. 12. The sensitivity curve of H_2PcSu in the dark has not been shown because of the instability of the response at higher NO_2 concentrations. The response of H_2PcSu under illumination is quite stable and seems to be useful for practical applications. The relative response magnitude S here is defined as

$$S = \frac{R_{\mathrm{exp}} - R_{\mathrm{before}}}{R_{\mathrm{before}}} \times 100 \qquad [\%]$$

where R_{before} is the resistivity before the gas exposure, R_{exp} – resistivity during the exposure.

4. Conclusions

We have observed that sulfonamide substituted phthalocyanines have quite high absorption coefficients and photoconductivities. Photoconductivity relaxation is slow; it can be explained by charge carrier trapping in deep traps. The Pcs under study are prospective materials for NO_2 sensors, capable of operating even at room temperature. Transmittance optical spectroscopy can be also used as a detection method but responses are weak. The electrical response in the dark is higher but its reaction and recovery times are slow. This leads to the shift of the baseline between the successive exposures. This problem can be overcome by sample illumination during the detection. The photoelectrical responses of H_2PcSu thin films under the NO_2 exposure are stable, quite fast and fully reversible. The profiles of the current changes for H_2PcSu and ZnPcSu are completely different, which suggests different mechanisms of the sensitivity to NO_2.

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