A low-symmetrical zinc phthalocyanine-based Langmuir-Blodgett thin films forNO_2 gas sensor applications

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Abstract. For many years effective detection of hazardous substances such as nitrogen oxides has remained a crucial task for environmental safety. In this article, we demonstrate high promising NO_2–sensitive Langmuir-Blodgett monolayer structures based on 2-((2′-hydroxymethyl)-benzyloxy)-9(10),16(17),23(24)-tri-*tret*-butyl- substituted low symmetrical zinc phthalocyanine complex bearing hydroxyl group on the periphery (compound **1**). Amphiphilic arrangement of macrocycles was demonstrated to eliminate disordered molecular aggregation, resulting in a marked NO_2 gas sensing effect under real atmospheric conditions. The optical response of monolayers was at room temperature, with the significant spectral changes being caused by the specific charge transfer process in phthalocyanine π-conjugated electronic system.

1. Introduction

As a result of increased toxic gas production in chemical industry and its influence on human health, an effective detection of CO_2, NO, NO_2, NH_3, and other toxic gases has become a crucial task in environmental safety. Commonly used gas sensors are based on chemiresistive oxide thin films [1,2]; however they have some drawbacks, such as low selectivity and high power consumption [3]. In contrast, organic optical sensors are potentially more selective and have faster response times. Optical gas sensors based on organic thin films can operate at room temperatures [3] without external thermal stabilization. Moreover, manufacturing of organic sensing thin films is potentially cheaper due to utilizing only aqueous solution techniques, such as spin-coating, drop-casting and Langmuir-Blodgett (LB). However, the stability of sensors and signal recovery should be specifically improved.

Phthalocyanines (Pcs) are eligible sensing materials for NO_2 detection. Pcs are thermally and chemically stable, environmentally friendly and easy to produce. They exhibit strong light absorption in UV and visible regions.

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It is known that interaction of NO_2 molecules with Pc macrocycles leads to reduction of Q-band absorption (600 – 700 nm) and an increase in the additional bands in the range of 500 – 550 nm as well as beyond 700 nm [4]. The similar changes can be also observed in absorption spectra during formation of charge-transfer (CT) complexes due to the interaction of Pcs with electron withdrawing molecules [4].

In this article, we demonstrate a recent study of NO_2 gas sensitivity towards monolayer structures based on low-symmetrical zinc phthalocyanine complexes.

2. Formation of monolayers

The synthesis of complex **1** was previously described [5]. For the preparation of LB films, KSV mini through system was applied. Ultrapure water with resistivity of 18 MOhm·cm was used as a subphase. The subphase temperature was regulated at 20°C by Julabo CD200F circulator. Complex **1** was uniformly spread from chloroform solution (100 µl of concentration $2 \cdot 10^{-4}$ M) onto the subphase. After evaporation of the solvent, the floating film was compressed at a constant rate of 5 mm/min until the surface pressure reached 20 mN/m (a value which corresponds to the linear region of the complex **1** compression isotherm). This value was held during the film transfer process onto hydrophilic glass substrate (KnittelGlaser 20x20 mm). The substrate was preliminary dipped into the water. The monolayer was deposited with constant transfer rate of 5 mm/min, with the monolayer transfer ratio being equal to 1±0.3.

3. Optical measurements and gas testing experiment

For spectral measurements of solution and thin film samples, a Perkin Elmer Lambda 1050 spectrometer was used. Experimental setup for gas testing is presented in Figure 1. The optical transmittance of the sample was measured during the gas exposure. In our experiments, NO_2 was diluted with N_2 as a carrier gas, with their ratio being carefully controlled to obtain the best response.

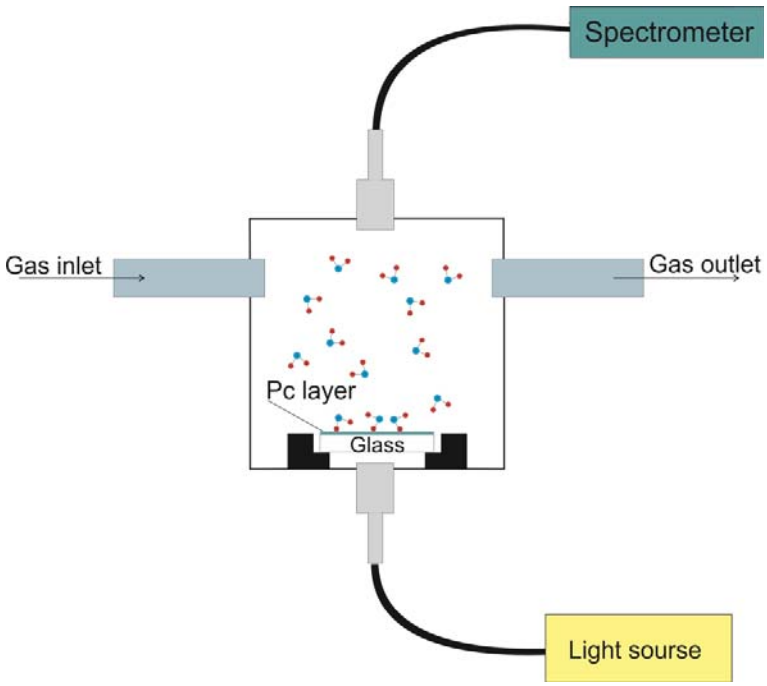

Figure 1. Scheme of experimental setup for gas sensing

4. Results and discussions

*4.1. Chemical structure and optical properties of phthalocyanine complex **1**.*

Chemical structure of complex **1** and DFT optimized geometry of a model based on this compound are presented in Figure 2. In this work, quantum chemical calculations were performed using density functional theory (DFT). The Perdew–Burke–Ernzerhof (PBE) functional [6] and PRIRODA software package, supplied with the cc-pVDZ basis set [7], were used for optimization of the model structure corresponding to the low-symmetrical phthalocyanine complex **1** in the steady state. *Tert*-butyl substituents were replaced with hydrogen atoms to reduce a calculation time. The valence shells were described by basis sets with the following contraction schemes: {6s2p}/[2s1p] on H; {10s7p3d}/[3s2p1d] on C, N, O; and (17s13p8d)/[12s9p4d] on Zn atoms respectively. Systematic vibrational analysis was performed to confirm whether an optimized geometry corresponds to a local minimum without imaginary frequencies.

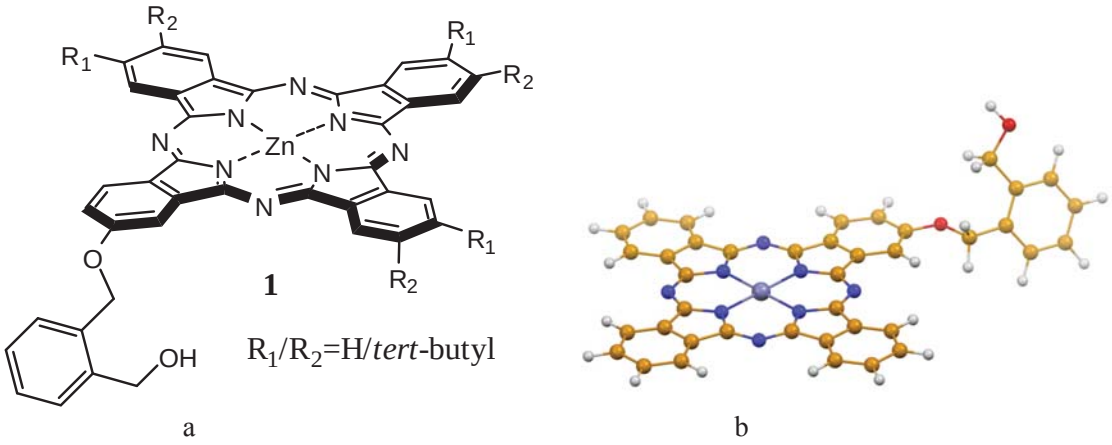

Figure 2. Phthalocyanine complex **1** (a) and DFT optimized (b) geometry of a model, in which peripheral alkyl substituents were replaced with hydrogens to reduce a calculation time

UV/Vis spectrum of complex **1** in chloroform (Figure 3a) contains three typical well-resolved absorption bands (λ_1=351 nm – Soret band, λ_2=614 nm – vibrational satellite of Q-band, λ_3=680 nm – Q-band). UV/Vis spectrum of monolayer film (Figure 3b) also exhibits three basic bands which have nearly the same position as the complex **1**.

The majority of phthalocyanines have a tendency to form H- or J-type aggregates in thin films caused by strong π-π intermolecular interactions. The molecular aggregation in thin films alters UV/Vis spectra dramatically – new blue-shifted (for H-aggregates) and red-shifted (for J-aggregates) bands toward the Q-band as well as considerable spectral broadening are typically observed. However, significant suppression of intermolecular interaction in LB thin film of compound **1** was demonstrated. The UV/Vis spectra of Langmuir monolayers and unsymmetrically substituted complex **1** from which they were derived (Figure 3) clearly indicate the significant decreasing in the aggregation behavior compared to the symmetrical analogs [8].

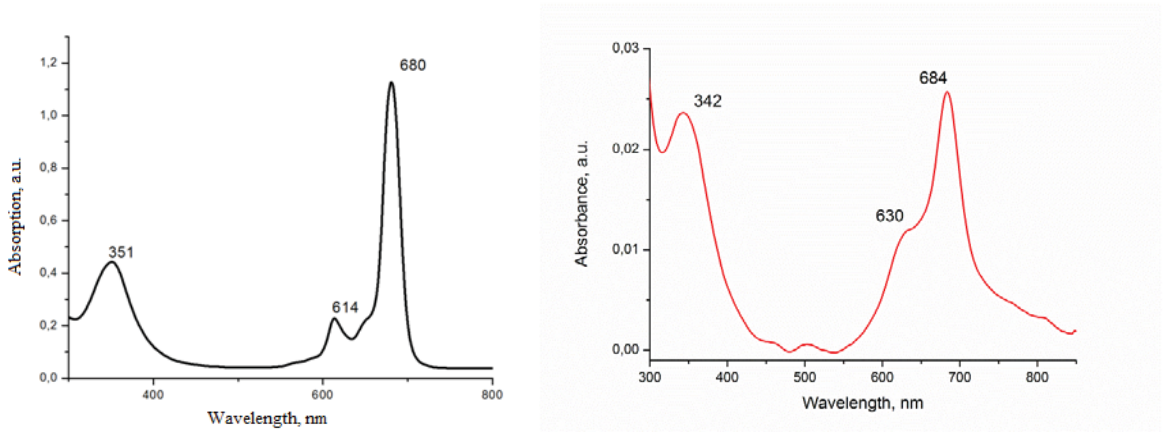

Figure 3. UV/Vis spectra of complex **1** in chloroform (a) and the LB thin film (b)

4.2. Spectral changes induced by NO_2 exposure

The interaction of NO_2 with the monolayer structure leads to appearance of a new peak at 506 nm and a decreasing the Q-band (Figure 4a). This may indicate a formation of the charge transfer complex of **1** with NO_2 molecule, describing a new band as the CT-band. In order to recover sensitive properties, we heated the film up to 150°C and held it for 10 minutes. The CT-band has disappeared demonstrating a desorption of NO_2 (Figure 4b). At the same time, heating reveals spectral changes in Q-band region (Figure 4a) which can be attributed to the reorganization of the macrocycles providing significant strengthening the H-type molecular aggregation. The similar facts were previously reported [9], demonstrating a method to produce density-packed phthalocyanine thin films [10].

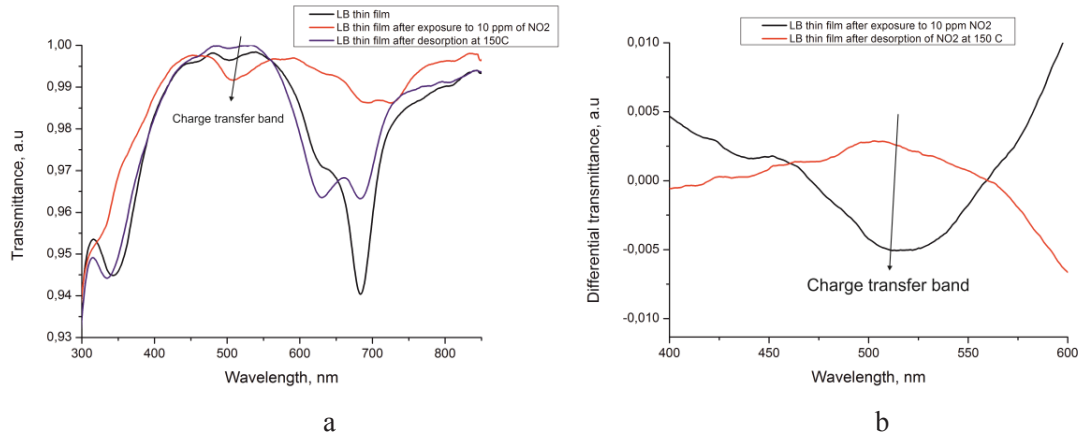

Figure 4 Linear (a) and differential (b) transmittance spectra of the LB thin film after exposure and desorption of NO_2

5. Conclusion

A low-symmetrical zinc phthalocyanine complex **1** bearing a hydroxy group on the periphery was used for the preparation of LB thin films to estimate a possibility of their use in optical gas sensing applications. Owing to the unsymmetrical structure, complex **1** has a tendency to form ordered monolayer structure on glass substrates. The interaction of NO_2 with the monolayer structure leads to dramatic spectral changings induced by formation of charge-transfer complexes. We demonstrated recovery properties of CT-band by utilizing of heating. Moreover, significant aggregation features of the macrocycles were also demonstrated on heating the structures.

Acknowledgements
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