Soluble phthalocyanines as optical gas sensing materials

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INTRODUCTION

Metal phthalocyanines (MPcs) are organic macrocycles with great technological importance for many different applications, owing to their interesting properties such as thermal and chemical stability, biocompatibility, electrical (semi)conductivity. Moreover MPcs films can be deposited by using a variety of techniques such as spin coating [1], Langmuir-Blodgett [2], vacuum evaporation [2] and glow discharge induced sublimation [3]. In the gas sensing field, the optical properties of MPcs films have been recently utilized for developing optical chemical sensors for the detection of volatile organic compounds (VOCs) [3], because the interaction between the VOC vapour and the MPc compound produces transitory changes of the MPc optical absorption.

In this work a new phthalocyanine, i.e. zinc phthalocyanine (sulfonamide) (ZnPcSu), has been synthesized and ZnPcSu films have been deposited by spin coating. The chemical properties of the ZnPcSu films have been investigated through FT-IR analysis.

The optical response of ZnPcSu samples was tested by measuring the light reflected by a ZnPcSu-coated silicon substrate exposed to alcohol-vapour-containing atmospheres. Methanol (MtOH), ethanol (EtOH) and 2-propanol (PrOH) were chosen for these first measurements owing to the great interest to the detection and monitoring of these alcohols in many different applications (e.g. food and beverage quality control).

EXPERIMENTAL

ZnPcSu was prepared by chlorosulfonating a zinc phthalocyanine and then by the reaction with the corresponding amine. The obtained ZnPcSu was dissolved in chloroform. The solution was deposited on Si substrate by spin coating technique for 15 sec at the speed 5700 rpm. Thin film was dried in air during 5 hours.

FT-IR spectra were recorded in the 4000 - 400 cm^{-1} range using a Jasco FT-IR 660 spectrometer with resolution of 4 cm^{-1}.

The experimental set-up for gas sensing measurements of ZnPcSu films is equipped with two mass flow controllers (HORIBASTEC SEC-E440J): the former allows to control the flow rate of alcohol-containing mixture between 1 and 1000 sccm; the latter controls the flow rate of pure nitrogen from 1 to 5000 sccm and it is used to suitably dilute the gas mixture to the desired composition. The optical set-up for measuring the changes of film reflectance upon alcohol exposure is constituted by a fiber optic reflection probe R600 (Ocean Optics inc.) connected to an optical spectrometer USB2000 (Ocean Optics inc., wavelength range: 200-850 nm). The fiber optic probe is connected to the analysis chamber too so that the probe tip is put in front of the ZnPcSu sample. The excitation signal is supplied from a DH-2000 light source (Ocean Optics inc.) constituted by a deuterium and a halogen lamp. The reflected light is dispersed by the spectrometer on an array of 2048 diodes. The control software of the optical spectrometer (OIBase32) allows to collect complete optical spectra at different vapour concentrations and also to perform dynamic tests by measuring the light yield at up to six selected wavelengths versus time and alcohol concentration. All the optical measurements were performed at room temperature.

RESULTS AND DISCUSSION

The basic characterization of the spin coated layer has been performed through FT-IR (Fig. 1). The peaks which characterize the ZnPc [4] are found in the spectra of ZnPcSu too. The difference of assignments among ZnPc and ZnPcSu [5] is determined by SO_2 group at 1387 cm^{-1} (asymmetric stretching) and 1159 cm^{-1} (symmetric stretching), by the bond C-N in secondary amine at 1254 cm^{-1} and by the stretching of methyl group at 2968 cm^{-1} and 2875 cm^{-1} (not shown in the Figure).

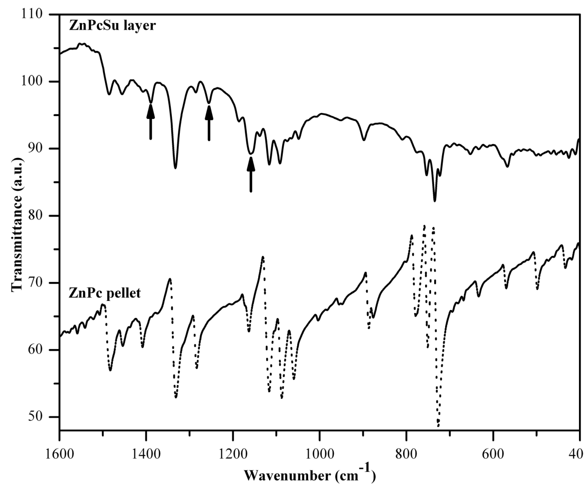

FIG. 1: *FT-IR spectra of ZnPc in KBr pellet (solid line) and spin coated layer of ZnPcSu (dot line).*

The optical response (in the 200 - 850 nm range) of ZnPcSu spin coated films was tested by exposing the samples to MtOH, EtOH and PrOH-containing atmospheres at different vapour concentrations. The first spectrum was acquired under a nitrogen atmosphere (I_{N2}) and the second spectrum under an atmosphere containing the alcohol vapour at the saturated vapour pressure ($I_{alcohol}$). The plot of the difference $\Delta I = (I_{N2} - I_{alcohol})$ between these two spectra is shown in Fig. 2 for all the three alcohols. In order to compare the intensity of the overall response to the three alcohols, it must be taken into account that the alcohol vapour concentration was different in the three cases, i.e.: $(13.3 \pm 1.1) \times 10^4$ ppm for methanol; $(5.8 \pm 0.5) \times 10^4$ ppm for ethanol; $(5.0 \pm 0.4) \times 10^4$ ppm for 2-propanol. By keeping in mind these values, one can conclude that the overall response of the sample is much more pronounced for EtOH than for MtOH and PrOH.

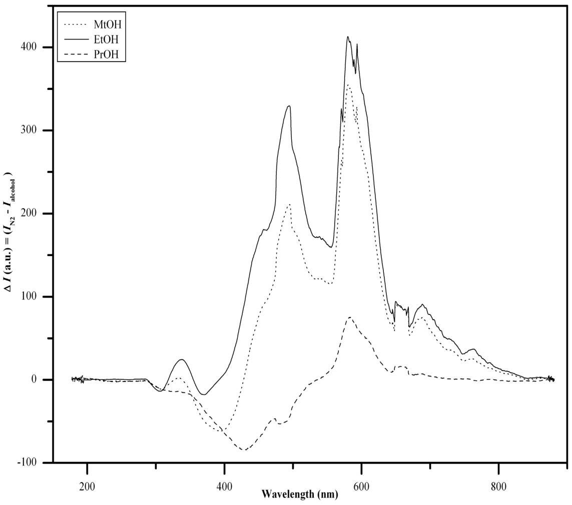

FIG. 2: *Change of the yield of the reflected light beam induced by the exposure of the ZnPcSu samples to the alcohol-vapour-containing atmospheres.*

Figure 3 displays the results of the first kinetic test, consisting in the measurement of the change of the light yield at 582 nm during repeated exposure-recovery cycles in atmospheres containing saturated alcohol vapours. The sample was exposed alternately to pure N_2 flow and to alcohol-containing flow (1000 sccm) for 6 min for each step.

The response and recovery values t_{50} shown in Table 1 characterize the ZnPcSu sample as a fast optical sensing material. The response time t_{50} is defined as the time taken for the signal intensity to reach the 50% its final saturated value during alcohol sorption and the recovery time t_{50} is defined as the time, which is taken for the signal intensity to get back to the 50% its saturated value in alcohol during alcohol desorption. The t_{50} times for both response and recovery phases are very short and their values are comparable for all the three alcohols.

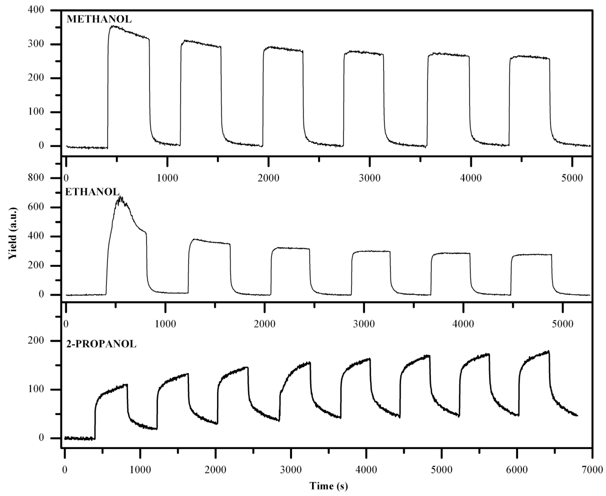

FIG. 3: Dynamic optical response of ZnPcSu sample in the presence of saturated alcohol vapour at fixed wavelength.

Gas	MtOH	EtOH	PrOH
concentration (10^4 ppm)	13.3	5.8	5.0
response time t_{50} (s)	3	3	3
recovery time t_{50} (s)	6	5	21

Table 1: Response and recovery times of ZnPcSu samples.

The main conclusion of this prefatory work is that the chosen soluble zinc phthalocyanine, which can be easily produced in the form of thin films by spin coating technique, is sensitive to different alcohol vapours (MtOH, EtOH and PrOH) and its fast response and recovery are very interesting for application of these films in gas sensors.

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