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Study of the sensor response of spun metal phthalocyanine films to volatile organic vapors using surface plasmon resonance

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Abstract

In this work, thin films of chloroaluminium phthalocyanine (ClAlPc), fluoroaluminium phthalocyanine (FAlPc) and fluorochromium phthalocyanine (FCrPc), which are insoluble in conventional solvents, were deposited by spin coating of their solutions in trifluoroacetic acid. The sensing response of these films versus acetic acid, three alcohols (methanol, ethanol, butanol) and three amines (methylamine, dimethylamine, trimethylamine) have been investigated using surface plasmon resonance as the sensing method. It has been shown that the sensor response of the investigated films decreases in the following order: acetic acid > alcohols > amines. The optical changes as monitored by SPR method have been used in conjunction with Fick's second law of diffusion to determine the diffusion coefficients of analyte vapor during the films' swelling process. The obtained results showed that the diffusion coefficients and the swelling characteristics of the films are dependent on the functional group of the phthalocyanine molecule and the molecular size of the analyte.

Keywords: Metal phthalocyanines, SPR technique, swelling, vapor diffusion

1. Introduction

Metal phthalocyanines (MPcs) consist of a central metal atom bound to a π -conjugated ligand where the physicochemical characteristics can be precisely altered by modifying the central metal atom as well as the peripheral substituents. Owing to their interesting distinctive properties, MPcs constitute one of the most studied classes of organic functional materials with potential application in many different areas. They have become a very popular choice of materials due to their varied electrochemical activity as well as their catalytic and unique optical properties. This extraordinary versatility makes them a very attractive class of materials for applications such as in nonlinear optics [1,2], solar cells [3,4], biosensing mediator [5], gas sensing [6,7] as well as in volatile organic compounds (VOCs) detection [8]. Research in the field of gas sensing has become an important issue during the last few decades as a result of increased awareness of the dangers of indoor and outdoor air pollution [9-11]. Toxic VOCs are one kind of these air pollutants, which are extensively used in paints, cleaning solvents, wood preservatives, plastics and cosmetics. Their vapors are highly toxic and their detection is therefore a very important challenge before they can reach critical levels in the environment. There is therefore an increasing demand to developing new gas sensors or improving the sensing properties of existing sensing materials. One essential concern of sensor research is to develop a sensing material with high sensitivity, excellent selectivity and complete reversibility. With this purpose in mind, much of the reported research was associated with the development of sensing materials with increased sensitivity to a specific target analyte. Organic materials are widely used as sensing material due their low cost, as well as the ability to tailor their chemical structures. Besides they can be processed as thin films using low-cost methods such as spin coating through solution transfer onto solid substrates. A vast range of synthetic organic materials has been investigated as active sensing layers; these include polymers [12], calixarenes [13], porphyrins [14,15] and phthalocyanines [16,17]. MPcs have attracted specific interest for gas sensing applications due to their high chemical and thermal stability as well as versatility of their structures [18]. While the majority of work is devoted to application of divalent metal phthalocyanines in organic electronic devices, a growing interest in trivalent metal phthalocyanines is also emerging. Halo-metallo(III)phthalocyanines (XM(III)Pc) exemplified by the axially ligated halide derivatives of aluminum, gallium, chromium and indium are non-planar by virtue of the axial halide atom which protrudes above the macrocycle ring. For example, the evaporated films of ClAlPc have been studied as humidity-selective sensors [19]. The sensitivity of devices versus

humidity, ammonia and ethanol has been investigated as function of analyte concentration and working temperature [20]. The behavior of ClAlPc films on exposure to NO₂, Cl₂ and NH₃ gases has also been investigated by Azim-Araghi and co-workers [21,22]. Chloroaluminum and fluoroaluminum phthalocyanines have been used together with C60 for the fabrication of planar heterojunction and blended organic photovoltaic devices [23-25]. The study of the photoconductivity changes of ClGaPc and ClInPc films has been employed in improving the detection of NH₃ and NO₂ [26,27]. Note that in all cited work thermal evaporation was used as a conventional method for the deposition of thin films of unsubstituted metal phthalocyanines.

In the present work, spin coating has been used to produce thin films of chloroaluminium phthalocyanine (ClAlPc), fluoroaluminium phthalocyanine (FAlPc) and fluorochromium phthalocyanine (FCrPc). The sensing properties of these films against organic vapors such as acetic acid (CH₃COOH), methanol (CH₃OH), ethanol (C₂H₅OH), butanol (C₄H₉OH), methylamine (CH₃NH₂), dimethylamine ((CH₃)₂NH) and trimethylamine((CH₃)₃N) have been investigated using surface plasmon resonance (SPR) method. This method is one of the most sensitive and remarkable technique in sensor studies which has invariably been shown to provide ultra-high-resolution transduction method [28]. The main challenge in this work lies in the fabrication of thin films of unsubstituted metal phthalocyanine molecules which are insoluble in conventional solvents using solution processing methods such as spin coating of their solutions in trifluoroacetic acid (TFA). The swelling characteristics of the studied films with regard to the molecular size of the examined analytes have been emphasized. This mainly ascribed to the high sensitivity of the SPR method of detecting optical parameters as well as thickness changes of organic films. The optical changes as monitored by the SPR method have been used in conjunction with Fick's second law of diffusion [29] to determine the diffusion coefficients of the analyte vapor during the swelling process. The obtained results showed that the diffusion coefficients and the swelling characteristics of the films are dependent on the functional group of the phthalocyanine molecule and the molecular size of the analyte.

2. Experimental details

2.1. Materials and film preparation

In this study, thin films of three different phthalocyanines (ClAlPc, FAlPc, FCrPc) were selected as active sensing layers. These phthalocyanine derivatives have been synthesized

according to the technique published elsewhere [30] and the chemical structures of the molecules are shown in Fig. 1. Solutions in TFA of the studied phthalocyanines have been prepared from powders of MPCs mixed with TFA in the concentration of $\sim 1 \text{ mg ml}^{-1}$. The mixtures were sonicated for 15 min and then filtered to obtain homogeneous solutions.

Thin films of MPCs were prepared via spin coating; 70 μl of each solution was dispensed onto a rotating substrate at various spin speeds (ω) in the range of 1000-3000 rpm to obtain films with various thicknesses. The rotation of substrates was continued for 60 s to allow evaporation of the solvent. Spun films were deposited onto glass slides for UV-vis absorption studies while 40 nm gold-coated glass slides were used for SPR measurements. Gold layers were deposited by thermal evaporation under vacuum of 10^{-6} mbar onto pre-cleaned glass slides at the rate of 0.2 nm s^{-1} .

2.2. Equipment and film characterization

UV-vis spectra were recorded with Varian Carry 50 Scan UV-Vis spectrophotometer in a range 300-900 nm. SPR measurements were carried out using a home-made setup utilizing Kretschmann's configuration [31]. Semi-cylindrical prism (refractive index of 1.515) and a He-Ne laser with the wavelength of 632.8 nm are used in the SPR system, which has already been described in a previous study [32]. SPR technique allows us to evaluate thickness and refractive index of thin films by fitting the SPR measured curves to Fresnel equations using Winspall 3.02 software (Max-Planck Institute [33]).

2.3. Sensor properties study

Vapor sensing properties of the MPC spun films were investigated by performing kinetic SPR measurements. For the kinetic measurements, a PTFE gas cell was sealed against the spun films using a rubber O-ring and placed on the internal rotating table of the θ - 2θ table and the reflected light intensity was measured as a function of time at a fixed angle of incidence during vapor exposures.

A group of amines (methylamine, dimethylamine, and trimethylamine), a group of alcohols (methanol, ethanol, and butanol) and an acid (acetic acid) vapors were chosen as analytes in order to compare the sensor responses and investigate the nature of interaction. The examined analytes were purchased from Sigma-Aldrich and used as sources to produce their vapors. Air was used as a diluent gas. Precise amounts of analyte solutions were transferred to a 2L glass

bottle using a microsyringe and were allowed to evaporate by gentle heating. The concentration of the analyte vapors was calculated according to the gas law [34]:

$$c = \frac{22.4\rho TV_s}{273MV} \times 10^3 \quad (1)$$

where c is the vapor concentration (ppm), ρ is the density of the liquid sample (g mL^{-1}), T is the temperature of container (K), V_s is the volume of the analyte solution (μL), M is the molecular weight of analyte (g) and V is the volume of the container (2L). In order to investigate the concentration effect on the sensing behavior, the analyte vapors were further diluted in a 50 mL syringe to obtain 200, 400, 600, 800 and 1000 ppm concentrations and then injected into the gas cell. Recovery of the sensing layers was examined by injecting fresh air into the gas cell. SPR curves were recorded before and after vapor exposure and then kinetic measurements were carried out. The kinetic responses were recorded by fixing the angle of incidence at a constant value which is on the linear region on the SPR curve and close to the resonance angle. Five different concentrations of the studied analytes vapor were injected into the gas cell and the reflected light intensity was recorded as a function of time. All exposure cycles were performed for 2 min followed by 2 min of dry air exposure to examine sensor's recovery. In order to clarify the adsorption and desorption processes the 1000 ppm concentration of vapors exposure was investigated in further detail.

3. Results and discussion

3.1 Characterization of spin coated films

Thermal evaporation is known to be a conventional method for the deposition of films of unsubstituted metal phthalocyanines [35]. In this work, thin films of ClAlPc, FAIPc and FCrPc were deposited by spin coating of their solutions in TFA. The deposition of some MPcs using their solutions in TFA has already been described in the literature [36,37].

Fig. 2 shows the UV-visible spectra of the MPc films spun at 1000 rpm. All materials exhibit two main Q and B bands typical for the electronic transitions of phthalocyanines. The Q-band in the UV-spectra of the films is broader than the corresponding band in the spectra of solutions where the individual molecules are present. This change is due to intermolecular interactions inducing the Davydov splitting of the bands corresponding to the allowed transitions [38]. Q-band in the spectra of ClAlPc solutions lies in the range from 670-685 nm

depending on the used solvent [39]. The UV-vis absorption spectrum of the spun CIAIPc film (Fig. 2a) is similar to those of the evaporated CIAIPc films, reported in the literature [40,41] and indicates the presence of the triclinic phase of CIAIPc in the film. A wide absorption Q-band in the region 600-800 nm with a maximum at about 760 nm is typical of triclinic CIAIPc films [40-44].

The Q-band in the spectrum of FCrPc film also demonstrates a red shift (Fig. 2c) relative to that in the spectrum of solution (672 nm). In contrast to CIAIPc the Q-band of FAIPc film is blue shifted to 656 nm (Fig. 2b) relative to that at 680 nm in the spectrum of its solution [25]. This blue shift might be attributable to the unique linearly stacked fluorine bridging structure of FAIPc and is consistent with absorption spectra of FAIPc films reported in the literature [45,46]. The presence of the second peak with a maximum at 680 nm indicates the presence of non-aggregated species. Increasing the spin speed gives rise to thinner films and therefore to a monotonic decrease of absorbance without any changes of the position and relative intensities of the band maxima.

Fig. 3 shows a set of experimental SPR curves of spin coated MPc films with different spin speeds. It is clearly shown that there is a remarkable shift of the SPR resonance angle (θ_{SPR}) for spin-coated films when they are compared with the SPR curve of bare gold film. Inset of Fig. 3 shows the linear increase in the shift of the resonance angle ($\Delta\theta$) with decreasing spin speed. This shift is directly related to the thickness and optical constants of the organic film deposited on gold surface and the relation can be described by the following expression [32]:

$$\Delta\theta = \frac{(2\pi/\lambda)(|\epsilon_m|\epsilon_i)^{3/2}d}{(n_p \cos\theta)(|\epsilon_m| - \epsilon_i)^2 \epsilon} (\epsilon - \epsilon_i) \quad (2)$$

where λ is the wavelength of the laser beam ($\lambda=632.8$ nm), n_p is the refractive index of the semi-cylindrical prism, $|\epsilon_m|$ is the modulus of the complex dielectric constant of the gold film, ϵ_i is the dielectric constant of the medium in contact with the film (which is air in our experiments), ϵ is the film's dielectric constant, and d is MPc film thickness.

The values of the resonance angle (θ_{SPR}), the SPR shifts ($\Delta\theta$) and thicknesses are summarized in Table 1 for all spun films. Winspill 3.02 software was used for the fitting of the experimentally measured SPR curves and it was carried out (film thickness of 40 nm was used to account for the reference SPR curve of bare gold film). Changes in SPR curve widths (ΔFWHM representing changes of full width at half maximum) are also given in Table 1.

Δ FWHM defines the magnitude of broadening of the SPR curve and it accounts for the damping in the resonance with increasing film thickness [47]. The width of the SPR curve can be affected by the homogeneity and uniformity of the surface of the film [32]. As seen in Table 1, thicker films obtained for samples spun at 1000 rpm have their SPR curves broadened by over 30%. In order to investigate the sensing behavior, films spun at 2000 rpm with a smoother surface were used as a model.

3.2 Vapor sensing properties

Figs. 4-6 display the kinetic measurements of films spun at 2000 rpm on exposure to 1000 ppm of organic vapors, where normalized reflected light intensity is plotted as a function of time. The responses against various concentrations (200-1000 ppm) of organic vapors are also included in the insets of these figures. On injection of vapors, films exhibited sharp increase in reflectivity for a few seconds and then decreased exponentially until reaching saturation. It is clear that the responses of the investigated films are fast and reversible against all vapors. The response and the recovery times are about a few seconds and the recovery is almost complete. The insets of Figs. 4-6 clearly show concentration dependence of the all sensing films.

The interaction mechanism between vapor and thin film can be described by three stages as adsorption, diffusion and desorption process. The first stage can be ascribed to surface adsorption, which causes sharp increase in reflectivity when vapor molecules introduced into the gas cell, followed by vapor molecules diffusing into the film structure. During the latter process thin films' response starts to settle down and this can be seen as a decrease in reflectivity until saturation is reached. The diffusion is a dynamic process, which consists of adsorption and desorption of vapor molecules until equilibrium. When dry air is injected into the gas cell, desorption of vapor molecules occurs until full removal of adsorbed molecules is reached and recovery is complete.

The magnitude of the sharp increase and the final saturated response depends on the type of vapor molecules. The sensing mechanism is a dynamic process that depends on different parameters such as thin film structure [10], central metal atom [48] and type and size of the analyte molecule [15]. As illustrated in Figs. 4-6 the sensor response of all investigated films decreases in the following order: acetic acid > alcohols > amines. In order to quantify the response, films' swelling behaviors have been investigated in more details.

The characteristics of swelling can be analyzed using the Fick's second law of diffusion. This law states that the rate of change in concentration with time is proportional to the rate at which the concentration gradient changes with the distance in a given direction. This law is applied to a plane sheet (the sensing layer) and solved by considering a constant diffusion coefficient; the following equation is obtained for describing the concentration changes with time [29].

$$\frac{C}{C_0} = \frac{x}{a_0} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} \sin \frac{n\pi x}{a_0} \exp\left(-\frac{Dn^2\pi^2}{a_0^2} t\right) \quad (3)$$

where a_0 is the thickness, D is the diffusion coefficient, C and C_0 are the concentrations of the diffusant at time $t=t$ and at $t=0$, respectively. x is the distance where C is measured. Concentration terms can be replaced with the amount of diffusant (M) by using the following equation [49]:

$$M = \int_V C dV \quad (4)$$

When Eq. (4) is considered for a plane volume element and substituted in Eq. (3) the following equation is obtained [29]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D \pi^2}{a_0^2} t\right) \quad (5)$$

where M_t and M_∞ represent the amount of diffusant entering the plane sheet at time t and at $t=\infty$, respectively. Eq. (5) can be simplified to take the following form with accuracy of 99% still preserved:

$$\frac{M_t}{M_\infty} = 4 \sqrt{\frac{D}{\pi a_0^2}} t_s^{1/2} \quad (6)$$

where t_s represents the swelling time and Eq. (6) is called early-time equation. This square root dependence of the amount of diffusant on swelling time can be used to investigate the swelling characteristics of the thin films.

The amount of the diffusant penetrating into the film (M_t) is expected to increase film's transparency resulting in less light scattering from the film and therefore the reflected light intensity I_{rf} is inversely proportional to M_t [50]. Thus Eq. (6) can be written as:

$$\left(\frac{M_t}{M_\infty}\right) \sim \left(\frac{I_{rf(t)}}{I_{rf(\infty)}}\right)^{-1} = 4 \sqrt{\frac{D}{\pi a_0^2}} t_s^{1/2} \quad (7)$$

where $I_{rf(t)}$ is the reflected light intensity at any time and $I_{rf(\infty)}$ is the reflected light intensity during the saturated response.

Fig. 7 shows the normalized intensity of reflected light versus square root of the swelling time according to Eq. (7). The values of diffusion coefficients (D_s) determined from $\left(\frac{I_{rf(t)}}{I_{rf(\infty)}}\right)^{-1}$ plotted as a function of $t_s^{1/2}$ are summarized in Table 2. The curves in Fig. 7 can be envisaged to have two different linear regions with two different slopes resulting in two different diffusion coefficients D_1 and D_2 . For instance in Fig. 7(a) these slopes are shown for acetic acid and it is clear that the diffusion coefficients are changing during the vapor exposure. Film's thickness after vapor's exposure have been estimated and summarized in Table 4. The increase in the thickness is ascribed to swelling of the films which obviously depends on the vapor diffusion into the film matrix.

Fig. 7(a) shows the responses of the three different phthalocyanine films to acetic acid. All three films exhibit the highest response to acetic acid among the studied analytes. At the same time ClAlPc film is the most sensitive to acetic acid compared to the other investigated phthalocyanines. Interaction between acetic acid and phthalocyanine films starts with a fast diffusion (D_1) and then reaches a saturation point with a lower diffusion coefficient (D_2). Acetic acid molecules penetrate into the film leading to film swelling. Films' thicknesses after each vapor exposure are estimated using the SPR curve data fitting and are summarized in Table 3. Similar behavior is observed in the case of methanol (Fig. 7(b)), however in the case of ethanol and butanol the diffusion coefficients are much lower (Table 2). The larger values of diffusion coefficient correspond to fast diffusion of the analytes. Acetic acid and methanol molecules have smaller length of alkyl chains than in the case of ethanol and butanol. The size

of analyte molecule is an important parameter for the sensor characteristics [15]. Smaller vapor molecules can easier diffuse into the film through the pores. Thus the diffusion coefficients of ethanol and butanol are lower than those of acetic acid and methanol. Although the size of acetic acid molecule is slightly larger than methanol, the response toward acetic acid is higher than that toward other analytes. This appears to be due to the ability of polar -COOH to form hydrogen bonds with Cl and F atoms of phthalocyanine molecules. In Fig. 7(c), amines have almost linear response during the exposure time while acetic acid and methanol have fast first encounter response. This also shows the lower interaction level between phthalocyanine molecules and amines. Although the molecular size of methylamine is nearly the same as the methanol's, sensor response however is much lower. That is mainly due to the effect of the different functional groups of the analytes; the functional group of alcohol vapors (OH) has a stronger interaction ability with the phthalocyanine molecules than the functional group of amines (NH₂). This tendency of interaction therefore gives rise to the level of response and its characteristics as illustrated in Fig.7 and Table2.

In order to characterize the sensing performance, the sensitivity (S) and the limit of detection (LOD) parameters were calculated using the Eq. (8) [51]. These parameters are summarized in Table 3.

$$\text{LOD} = \frac{3\sigma}{S} \quad (8)$$

where σ is the standard deviation of the signal and S is the sensitivity to a specified analyte, defined as the change of reflected light intensity per ppm (ppm⁻¹).

4. Conclusion

In this study the diffusion process of organic vapors in thin films of metal phthalocyanines has been analysed and discussed. Three different metal phthalocyanines were used for the active layer of vapor sensor and solid-state film transfer process was successfully achieved via spin coating technique. The films thickness was found to depend on the spin speed and was evaluated between 3.3-12.1 nm. MPC films were exposed to different concentrations of VOCs (acetic acid, methanol, ethanol, butanol, methylamine, dimethylamine and trimethylamine). The response of the sensing material was monitored by SPR system and the data were recorded as time-dependent optical changes. MPC films exhibited an excellent selectivity to

VOCs. All examined analytes have resulted in good sensor responses which were found to be fast and reversible. All examined MPc films were shown to be more sensitive to acetic acid and methanol vapors and are dependent on analyte concentration. In order to investigate the interaction between the MPc films and vapor molecule films' swelling was examined in terms of analytes diffusion coefficients. Our results showed that the functional group and molecular size of the analyte molecules can have detrimental effect on the sensor response. With the help of these promising results, understanding the diffusion process of vapors can be a key point of improving more selective vapor sensors.

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Figure Captions

Fig. 1: Chemical structure of the phthalocyanine derivatives ClAlPc (X=Cl, M=Al), FAIPc (X=F, M=Al), FCrPc (X=F, M=Cr).

Fig. 2: UV-vis absorption spectra of ClAlPc (a), FAIPc (b) and FCrPc (c) films spun at 1000 rpm.

Fig. 3: SPR curves of (a) ClAlPc, (b) FAIPc and (c) FCrPc spun films as a function of internal angle.

Fig. 4: The kinetic measurements of ClAlPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

Fig. 5: The kinetic measurements of FAIPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

Fig. 6: The kinetic measurements of FCrPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

Fig. 7: Plot of reflected light intensity against square root of swelling time for (a) acetic acid vapor, (b) alcohol vapors and (c) amine vapors.

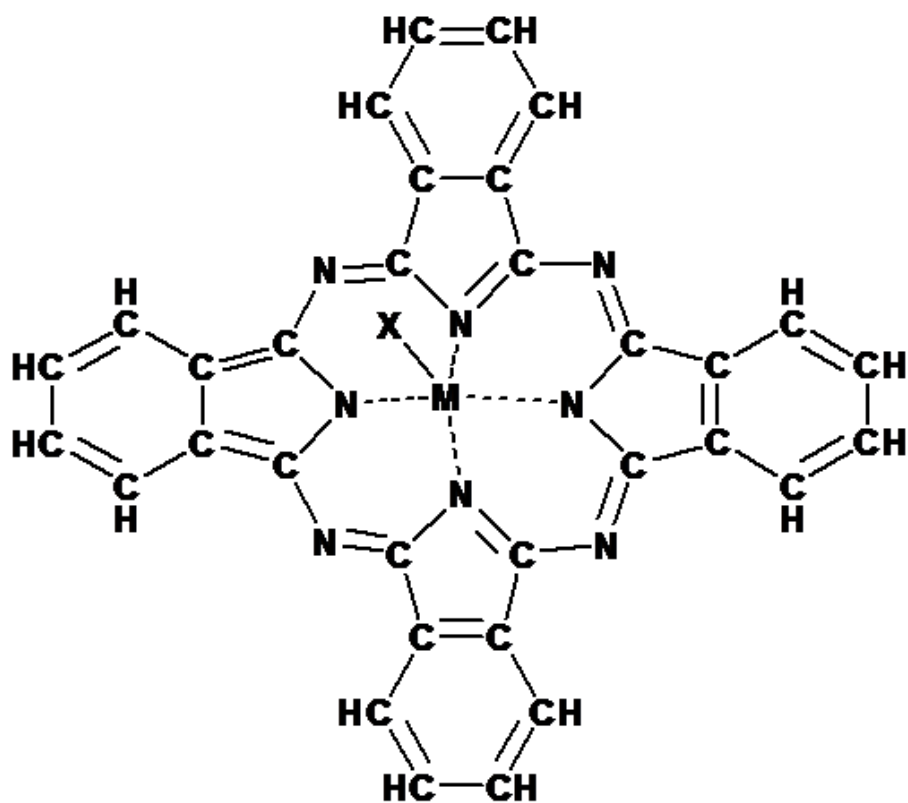


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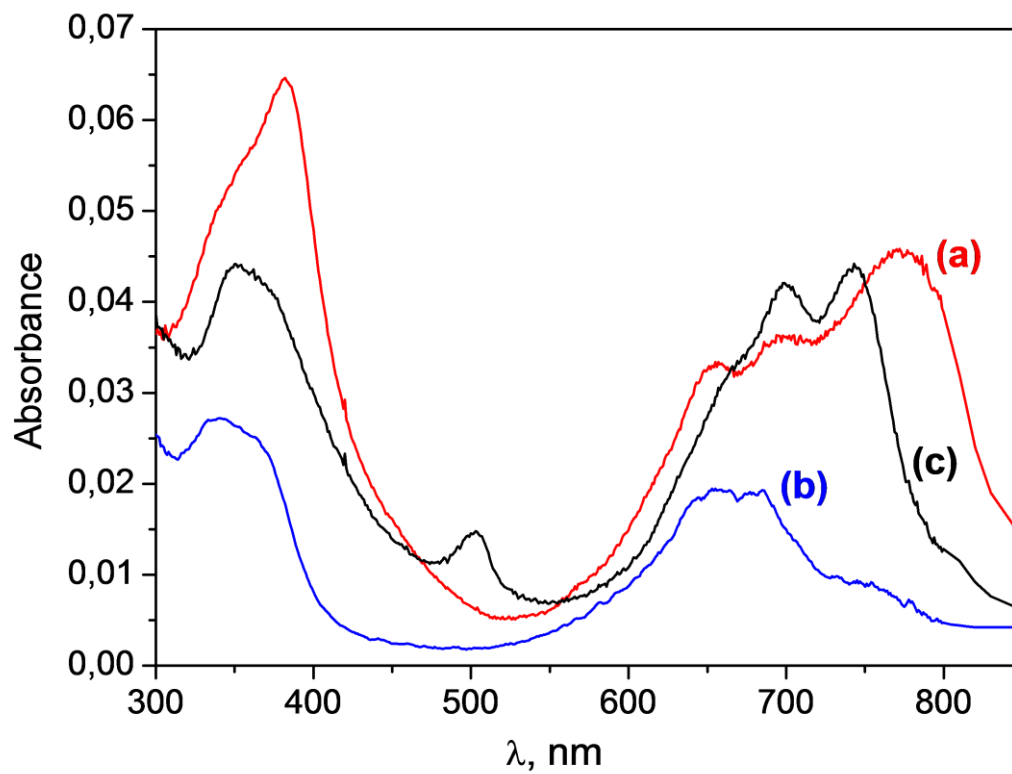


Fig. 2: UV-vis absorption spectra of ClAlPc (a), FAIPc (b) and FCrPc (c) films spun at 1000 rpm.

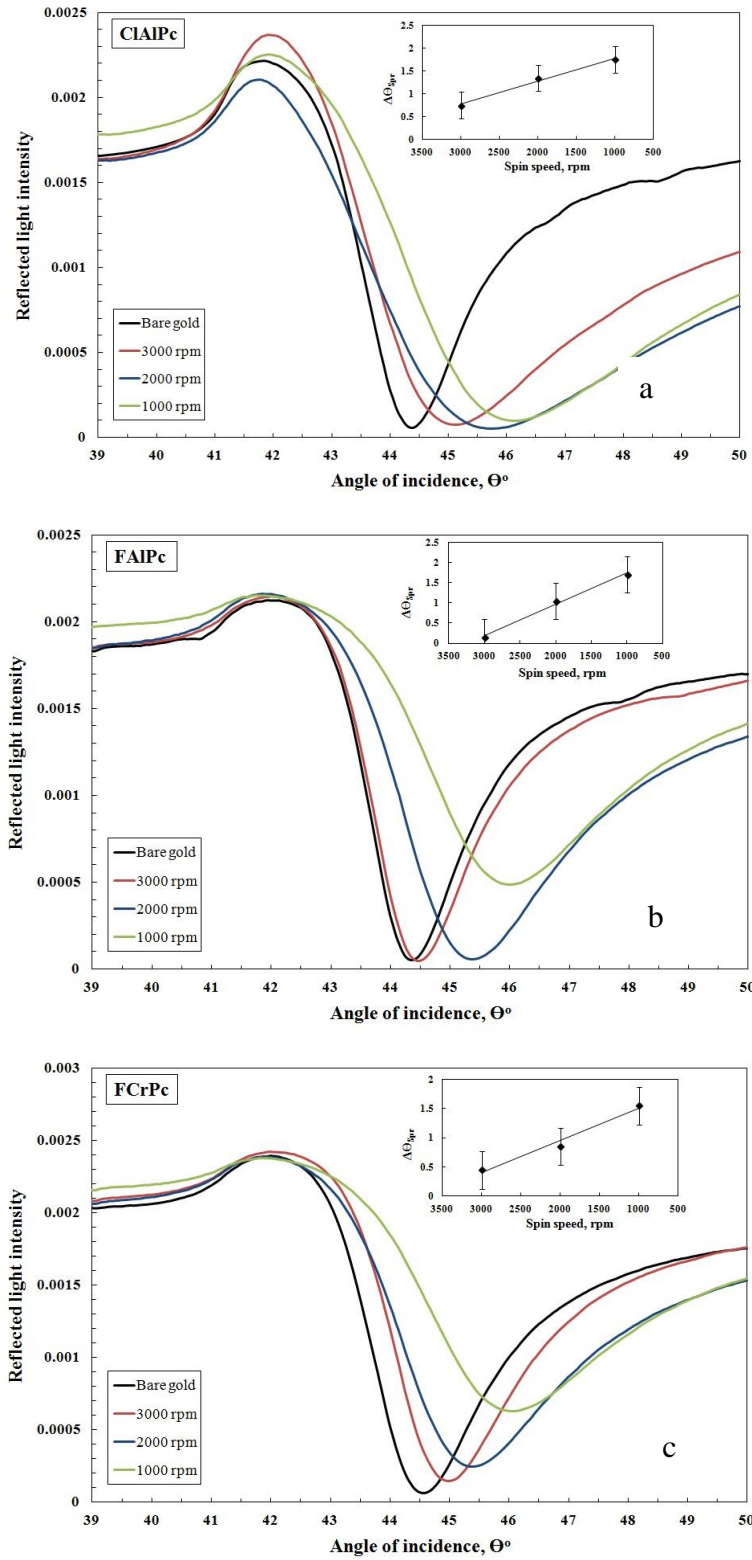


Fig. 3: SPR curves of (a) CIAIPc, (b) FAIPc and (c) FCrPc spun films as a function of internal angle.

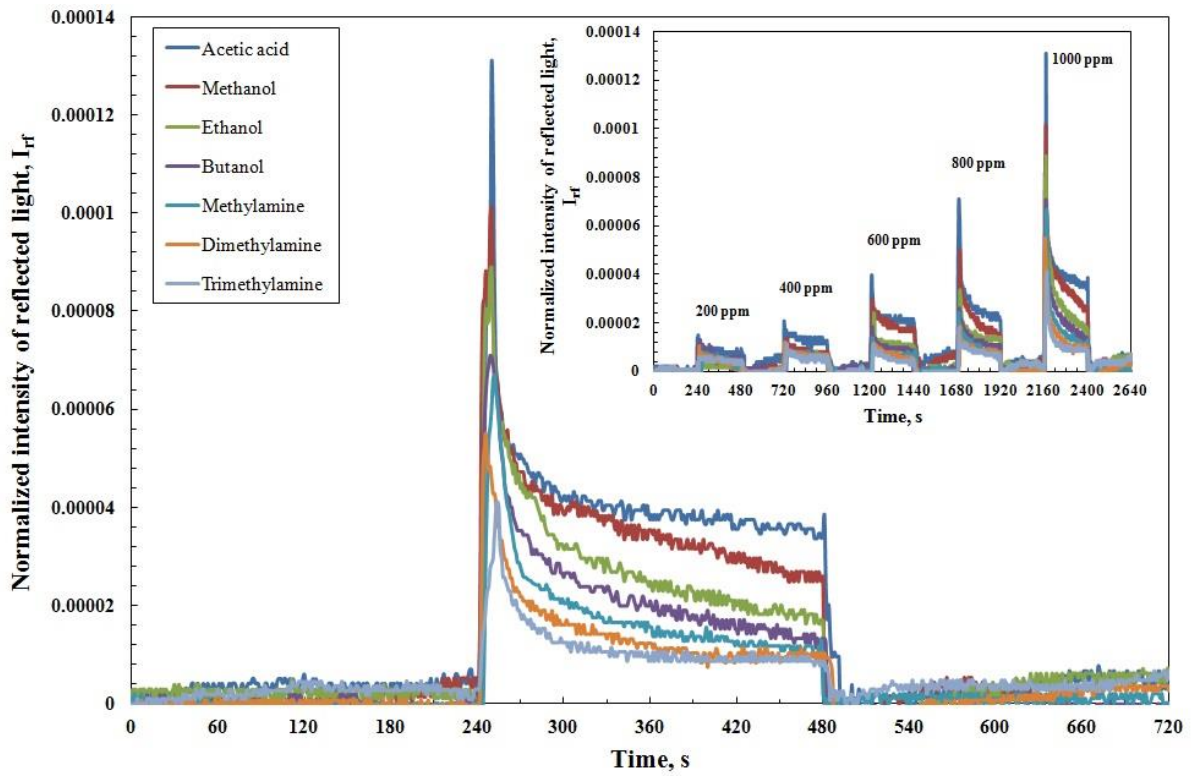


Fig. 4: The kinetic measurements of ClAlPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

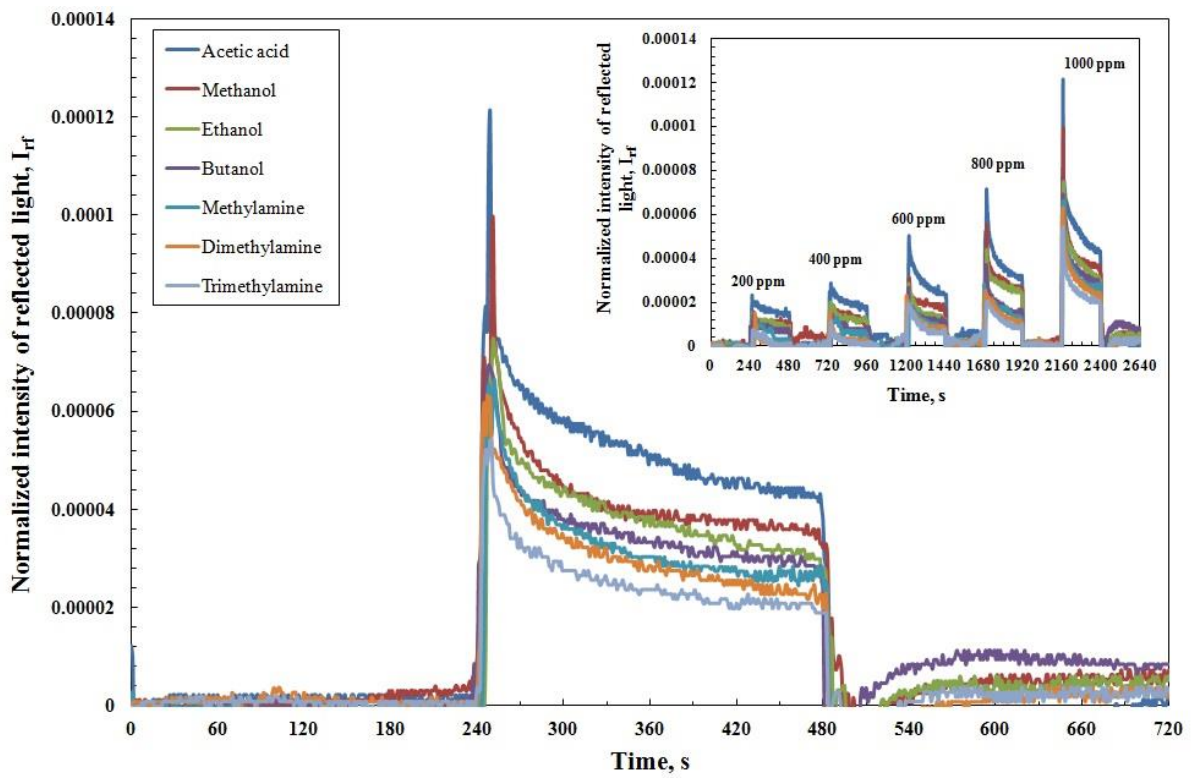


Fig. 5: The kinetic measurements of FAIPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

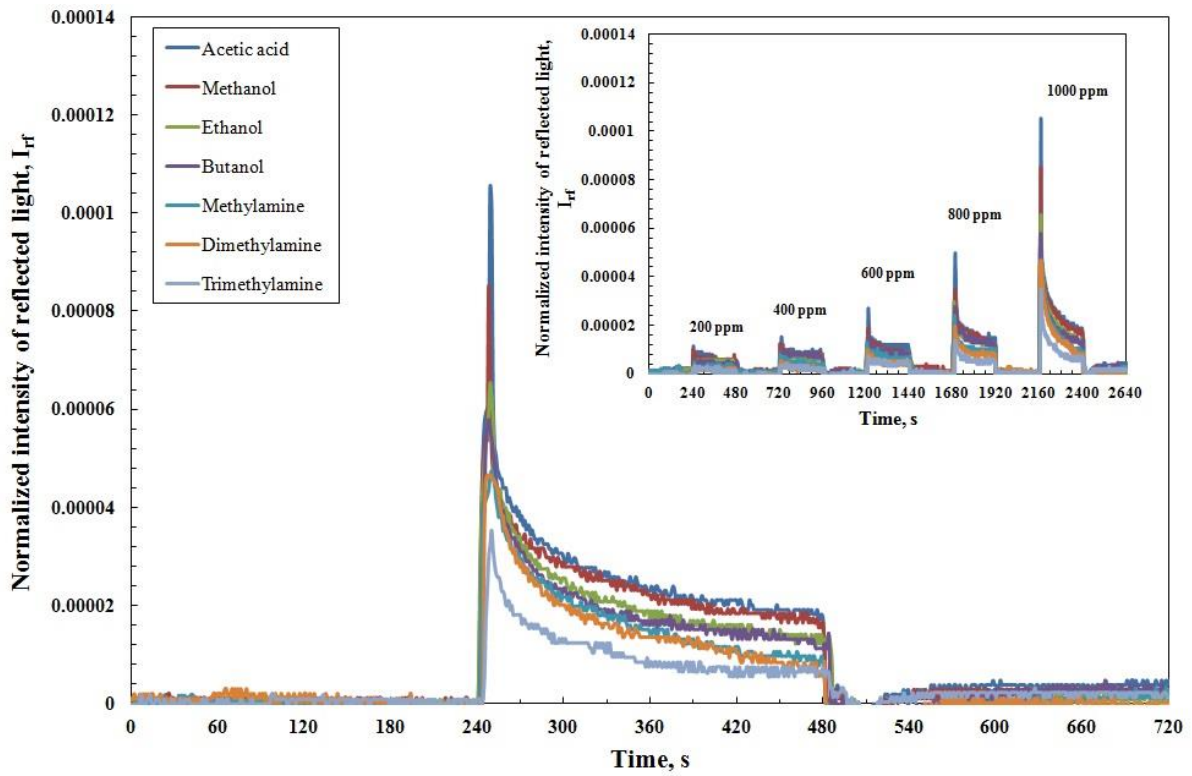


Fig. 6: The kinetic measurements of FCrPc spun films against 1000 ppm organic vapors (inset: reproducibility of the film for five different vapor concentrations).

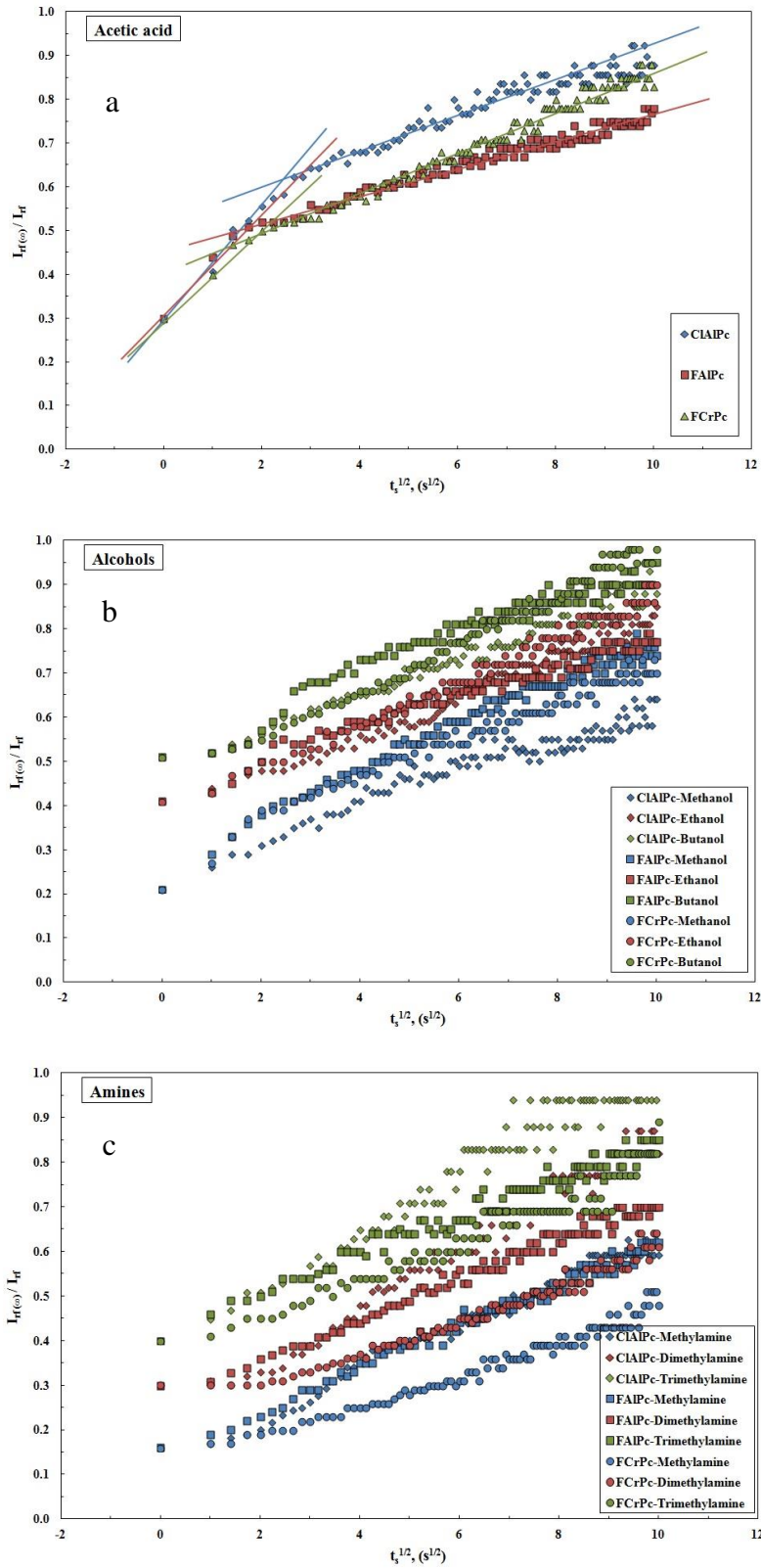


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