Chemsensor of NO$_2$ Gas Based on Porphyrin of 5, 10, 15, 20-Tetraphenylporphyrin LB Films and LS Films

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The sensitivity of 5, 10, 15, 20-tetraphenylporphyrin (H$_2$TPP) to the presence of NO$_2$ gas in diluted solutions and in Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) films was investigated by UV-visible spectroscopy. The shift of Soret and Q bands were analyzed and the energies involved were calculated. The exposure of LB porphyrin films deposited onto glass slides to NO$_2$ has performed as an active chemsensor with 7000 ppm gas concentration. Furthermore, the UV-vis dichroism absorption results associated with the Soret bands have given evidence of the tilt angle of the macrocycle related to the substrate. H$_2$TPP in LB film was tilted by an angle of $51 \pm 5°$ and in the LS film was tilted by an angle of $36° \pm 5°$ indicating the formation of a preferential organization of the molecular films depending on the deposition method.

1. Introduction

Tetraphenyl porphyrins or H$_2$TPP are the simplest porphyrins which have been investigated. These porphyrins yield isotherms with an extrapolated area of only 13-17 Å^2 per molecule[1]. This contrasts with an expected value of 225 Å^2 per molecule, if the molecules lie flat on the water surface, and with an expected value of 90 Å^2 per molecule for a vertical packing array of molecules[2]. For these macrocyclic molecules, organized supramolecular structures can be formed in monolayers. Such is the case in Langmuir-Blodgett (LB) monolayers and self-assembled monolayers (SAM), in which the macrocycles arrange themselves in a parallel alignment due to the inherent organization of the macrocyclic rings. The presence of double-conjugated bonds attributes the sp^2 planar configuration with several possibilities of π-π* transitions. These structures, referred to as a playing-card model, have been confirmed by AFM measurements of Langmuir and self-assembled monolayers of porphyrins and phthalocyanines[2]. The substantial attractive π-π interaction between porphyrin macrocycles may cause significant pre-aggregation prior to the compression of the film forming domains[2,3]. Furthermore, the limitation of 3D conformation due to the planar structure restricts the overall mobility on reaching a thermodynamic energy minimum.

Many free-base porphyrins have been studied as potential NO$_2$ sensors because they possess distinctive UV–vis absorption spectra due to their highly conjugated π-electron systems [4]. These sensors reliant on changes in the optical properties of the active sensing material, generally operate at room temperature and remain relatively immune to interference effects[5]. The optical responses toward alcohol vapors of H$_2$TPP and its derivatives suggested different molecule organization between spin coated and vacuum evaporation technique thin films[6]. Hence, supramolecular assemblies of porphyrins have been extensively studied for two main kinds of applications: for mimicking natural photosynthesis process and as components in molecular devices. The porphyrin orientation and the distance between the rings in monolayer and films are two important parameters for the interactions between the rings[7].

Based on the lower than expected area/molecule values, it can be concluded that in general the material must form multilayer stacks in which the structure and stability of the film (collapse 40 mNm^{-1}) is governed mainly by molecular packing rather than by hydrophilic/hydrophobic interactions [1-3,7]. The exposure of porphyrins to oxidizing or strong reducing gases induce dramatic change in the UV-visible absorption spectrum (Soret and Q bands) that are associated with $\pi \rightarrow \pi$* transitions and provide the basis for a remarkably interesting gas sensing capability[8,9].

The organization of supramolecular assemblies of H$_2$TPP films and its derivatives are dependent of subphase temperature and subphase modifications[2-3,7], such as the addition of different electrolytes[7] or changes in pH[10]. Moreover, the interaction of central metal and side-group substituents with weak and strong carboxylic acids by UV-vis spectroscopy were previously reported[11]. The UV-vis absorption circular or linear dichroism can also be used to estimate the orientation angle of the porphyrin rings with respect to the normal angle of the substrates in Langmuir-Blodgett (LB), Langmuir-Schaefer (LS) and self-assembled films[2,12-16].
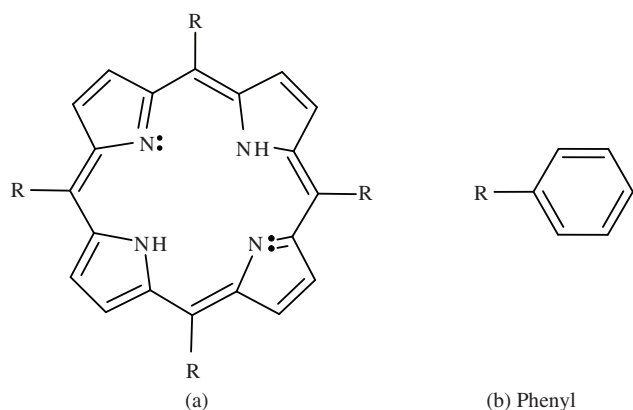
The goal of the present study was to investigate the optical absorbance behavior of H$_2$TPP in solution and in LB and LS films by UV-vis spectroscopy when exposed to NO$_2$ gas. The characteristics for gas sensing associated with sensitivity and response were analyzed by following the changes in the Soret and the Q bands. The concentration of the porphyrin and the subphase pH were used as major parameters for controlling the final aggregation state of molecules for chemsensor applications.

2. Materials and Methods

2.1. Materials

H$_2$TPP (Sigma Aldrich) is a derivative of free-porphyrin (Figure 1a) having a benzene group attached to the periphery of the ring system (Figure 1b). Chloroform p.a. (Merck) and hexane p.a. (Sigma, spectroscopic grade) were used as spreading solvents. Hy-

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Figure 1. a) Free-base porphyrin macrocycle and b) H$_2$TPP.

(a)

(b) Phenyl

(a)

(b)

Figure 2. The direction of polarized light incident on substrate a) and space coordinates (x, y, z) for expressing porphyrin orientation and b) Y-axis: dipping direction, Z-axis: normal to substrate, n-axis: centre axis of porphyrin molecule represented by circular plate.

drochloric acid (Synth) and sodium hydroxide (Sigma Aldrich) were used for pH adjustment. Quartz plates (SPI Supplies,USA) were made hydrophilic by immersion in hydrogen peroxide (Cromato Produtos Químicos Ltda, 30%v/v).

2.2. Measurements of δ-A isotherms and preparation of LB films at water interface.

The measurements of surface pressure-area (π-A isotherms) were carried out at a temperature of 23 ± 1 °C on a Nima model 311D Langmuir trough with a Wilhelmy plate balance. The trough and the barrier are made of Teflon®. The quality of the spreading solvent and subphase was tested by compressing the interface after the spreading and evaporation of the solvent. The final surface pressure was always lower than 0.2 mN·m⁻¹ assuring no contaminate residues. Distilled water further purified by a Milli-Q system (>18.2 MΩ·c) was used as subphase after the pH adjustment.

H$_2$TPP was dissolved in n-hexane/chloroform (in volumetric proportion of 6/4), and the concentration of H$_2$TPP in the solution was 30 μM. The solvents were allowed to evaporate for about 20 minutes and the barrier was compressed at constant rate of 7.8 Å²·min⁻¹.molecule⁻¹.

Langmuir-Blodgett (LB) films were prepared by the immersion of pre-treated hydrophilic quartz plates through the H$_2$TPP monolayer-subphase interface maintained at 18 mN·m⁻¹ for different solution concentrations. In the sequence, LS films were deposited by manual immersion after extraction of LB film and surface pressure stabilization was reached. These samples were characterized by Ultraviolet-visible (UV-vis) spectroscopy measurements.

In order to obtain a hydrophilic surface, quartz plates (1.0 x 9.75 x 25.4 mm) were treated with hydrogen peroxide at 60 °C for 30 minutes and then dried in an oven (at 60 °C for 24 hours).
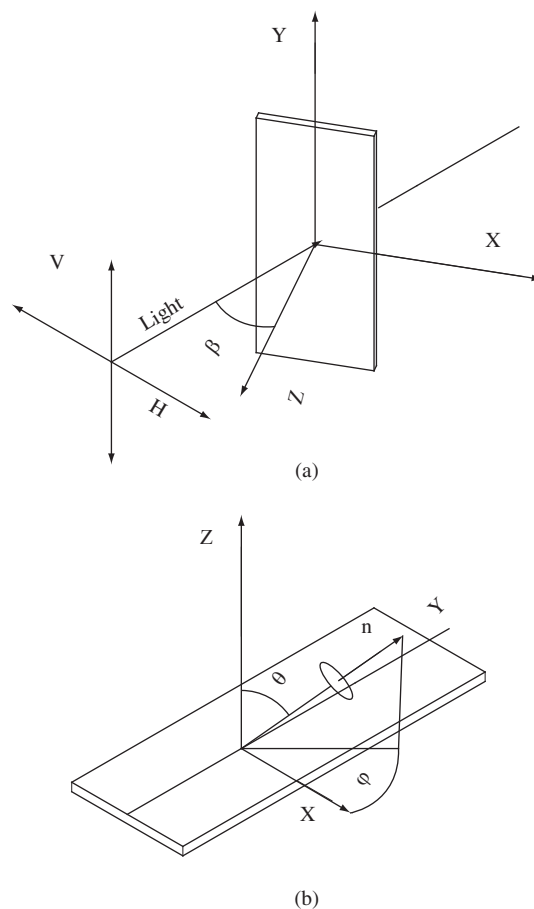
ACD/ChemSketch software (Advanced Chemistry Development, Inc, version 11.01) was used to estimate the value of area/molecule assuming a flat film formation (space-filled models).

2.3. Measurements of UV-vis spectra

UV-vis spectra were recorded on a Perkin Elmer Lambda EZ210 Spectrophotometer. Empty cuvette was used as the reference. The spectra were collected at 200 nm/min over a range of 300-900 nm, resolution within 2.0 nm.

2.4. Molecular orientation of phorphyrin in LB and LS films

The orientation of porphyrin molecules in LB and in LS films was investigated by polarized UV-vis absorption spectroscopy. Figure 2a and Figure 2b show 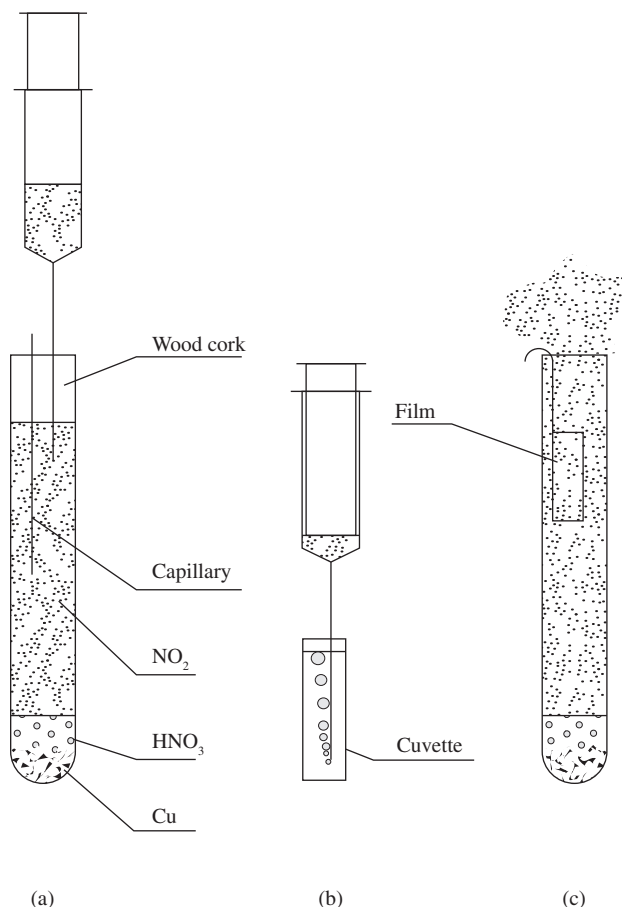the space coordinates (x, y, z) for expressing the porphyrin orientation and the direction of the incident polarized light on the substrate.

The optical absorption dichroism was used to study the orientation of the porphyrin rings relative to the normal direction of the substrate by measuring the dichroic ratios D$_β$, D$_β$ = A$_v$/A$_h$; where β is the angle of incident light regarding to the x-y plane, usually β = 0° and 45°; the A$_v$/A$_h$ parameter is calculated through the ratio of absorbance values from the film submitted to polarized light with electric vectors parallel and perpendicular to the dipping direction, respectively[2,12]. The dipping direction for LB films is generally considered to be the y-axis.
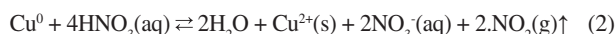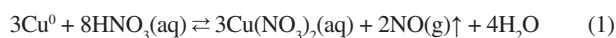
2.5. Gas sensing test

The configuration and setup for NO$_2$ synthesis apparatus is illustrated in Figure 3a. Experiments involving the bubbling of gas were conducted using an assay tube ("reactor") sealed with a wooden cork and two capillary, one for pressure equilibrium and other for the withdrawal of gas with a syringe. The just produced NO$_2$ gas was then injected into a standard UV-vis cuvette of 10 mm path length (Figure 3b). Alternatively, LB and LS films were exposed to the NO$_2$ gas at saturated concentration after opening the reactor and properly placing the film samples into the recipient (Figure 3c).

The production of NO$_2$ starts with the reaction of copper (Cu⁰) with concentrated nitric acid. Initially, the produced gas (NO) is colorless, that immediately reacts with the contained air inside the

Figure 4. π-A isotherms of H$_2$TPP, spreading solution concentration 30 μM: a) pH = 5 and b) pH = 8.

porphyrin structure, the two pirrolenine nitrogen atoms bearing lone pairs of electrons (pK$_b$ ~ 9) can be easily protonated with acids such as trifluoroacetic acid[11]. Porphyrins can be considered amphoteric compounds having both acidic (NH-acids) and basic (N-base) properties at the same time. Nitrogen atoms of imine type (-N=) are able to accept surplus protons, whereas pyrrole type nitrogen atoms (N-H) are able to donate protons. In fact, the ionization and acid-base properties of tetrapyrrolic compounds include the formation of anionic and cationic forms, i.e. processes that involve charge changes. Hence, the isotherm results are supported by considering a different packing of H$_2$TPP films at the air-subphase interface. That means, H$_2$TPP films are sensitive to acid (pH = 5) and alkaline (pH = 8) subphase solution due to the overall protonated-deprotonated charge balance[17].

Porphyrin derivatives very usually form 3D aggregates or multilayer with the porphyrin core tilted with respect to the water surface[2]. The results have shown that it is possible to obtain high values of area/molecule (not shown), ranging from 160 to 300 Å^2·molecule^{-1} for H$_2$TPP concentrations below 60 μM which are equivalent to the area value of 225 Å^2·molecule^{-1}, calculated via simulation model assuming H$_2$TPP molecules arranged in horizontal form (ChemSketch software). This result indicates the possibility of a flat film formation at air-water interface.

3.2. UV-vis absorption spectra of solution and LS film

The NO$_2$ gas bubbling experiment was used to identify the potential for the H$_2$TPP macromolecule to act as a chemical sensing material. The optical absorption spectrum of H$_2$TPP solution, before bubbling with NO$_2$, exhibits a sharp and intense absorption band around 417 nm (Soret band), and four bands of lower intensity and longer wavelength at 513, 548, 590 and 645 nm (Q bands) (Figure 5a). After NO$_2$ exposure, the Soret band shifted to red (Figure 4b) with a decrease in the energy of about 0.15 eV (Table 1), and the bands at 513 and 548 nm decreased in intensity. The bands at 590 and 645 nm shifted to red and other bands developed at around 603 and 655 nm (Figure 5b inset). In this work the NO$_2$ gas concentration was estimated to be about 7000 ppm based on stoichiometric calculation assuming 100% reaction conversion. In H$_2$TPP solution, the Soret peak appears at 417 nm and after the bubbling experiment the Soret band has changed to 439 nm. It was possible to identify this isobestic point as the intersection between the spectra before and after exposure to the gas. Further studies need to be conducted in order to investigate the sensitivity of H$_2$TPP films submitted to different NO$_2$ concentrations and maybe its correlation. Analogous study from Dunbar and co-workers[4] reported the kinetics response of Soret band absorption for the 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)

(a)   (b)   (c)

Figure 3. Schematic representation of bubbling experiments and the exposure of cast films to NO$_2$.

reactor producing the NO$_2$ (brown color) according to the following reactions at 25 °C: (Equations 1, 2 and 3):

$$3Cu^0 + 8HNO_3(aq) \rightleftarrows 3Cu(NO_3)_2(aq) + 2NO(g)\uparrow + 4H_2O \quad (1)$$

$$Cu^0 + 4HNO_3(aq) \rightleftarrows 2H_2O + Cu^{2+}(s) + 2NO_3^-(aq) + 2.NO_2(g)\uparrow \quad (2)$$

$$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)\uparrow \quad (3)$$
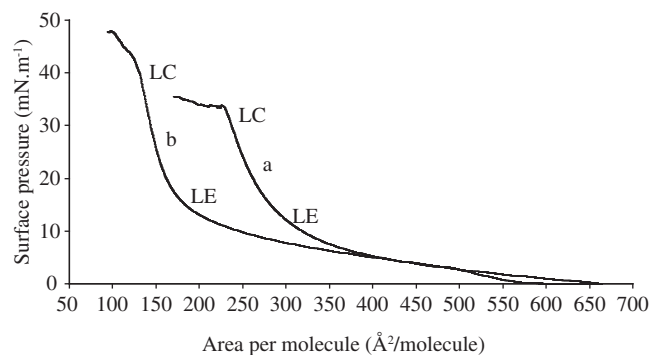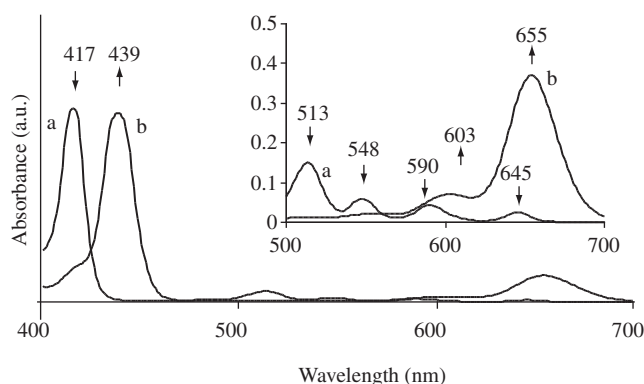
The relationship between NO$_2$/NO was not of major concern in the experiment since the oxidative environment used (excess of oxygen) has driven the equilibrium to NO$_2$ gas formation (reaction 3).

3. Results and Discussion

3.1. π-A isotherms and LB film deposition

Figure 4 shows the surface pressure–area isotherms for H$_2$TPP with concentration of 30 μM and pH = 5 (Figure 4a) and pH = 8 (Figure 4b).

The surface pressure-area isotherms (π-A) for H$_2$TPP films have shown typical curve profile associated with the presence of three main phases: G (gas phase), LE (liquid-expanded phase) and LC (liquid-condensed phase). The high value of projected area/molecule was obtained by using pH = 5.0 ± 0.1 with good range of control on film formation[17]. It can be understood that pH alters the charge balance in the macrocycle ring, mainly associated with the interaction between H$^+$ and the non-bonding electronic pair in nitrogen. In the

Table 1. Electronic spectra of H_2TPP film solutions before and after NO_2 exposure.

Sample	Soret band (nm)	Q(0.0) band (nm)	Q(0.1) band (nm)	Q(1.0) band (nm)	Q(1.1) band (nm)
Solution	417	513	548	590	645
LS film	439	N.A.	N.A.	603	655
$\Delta\lambda$(nm)/ ΔE(eV)	22/-0.15	N.A.	N.A.	13/-0.05	10/-0.03

N.A – Not applicable.

Figure 6. UV-vis spectra of LS H_2TPP films (2 layers) deposited onto quartz substrate at pH = 5, exposed to NO_2 gas at different times.
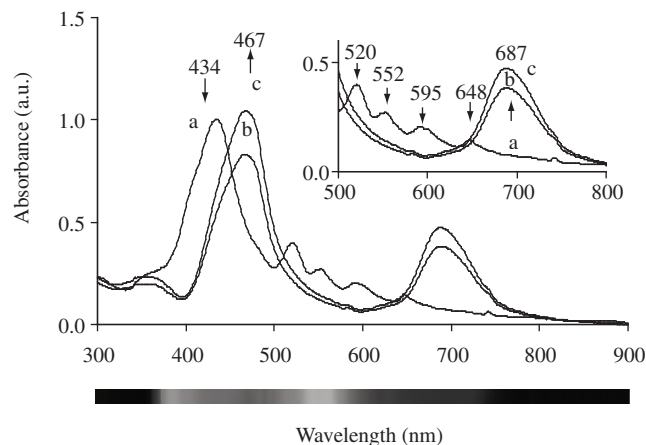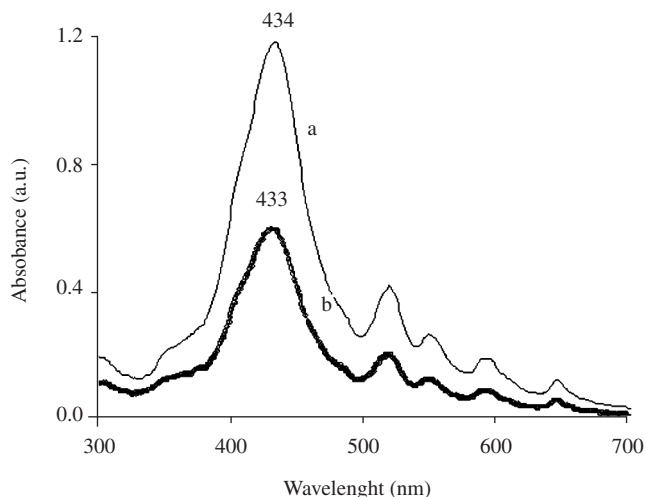

Figure 5. Optical absorbance spectrum of 5×10^{-6} M solution of H_2TPP, a) before and b) after exposure to NO_2 saturated gas. Soret Band and Q bands (insert).

Figure 7. UV-vis spectra of H_2TPP films (2 layers) deposited onto quartz substrate at pH = 5, a) LS film and b) LB film.

phenyl]-21H,23H-porphine (EHO) films that improved dramatically when the samples were exposed to NO_2.

The absorption Soret band of the film, presented a red shift in comparison with solution form (417 to 434 nm). The Soret band in the film is broader than in the solution with an average bandwidth of 168 nm compared to 142 nm in solution. This is attributed to the crystal field effect for the relatively closely packed porphyrin molecules in the thin film assembly[9]. Following the transference of H_2TPP onto a quartz plate, the Soret and Q bands were studied by exposing the samples (LB and LS) to the gas. The same sample of LS film was exposed to the NO_2 in a test tube in steps of 4 seconds, totalizing 16 seconds of exposure. The effect of exposing the LS film of H_2TPP (two layers, deposited at 30 μM concentration) to NO_2 was a red shift of 33 nm of the Soret band (434 to 467 nm) (Figure 6), followed by a simultaneous disappearance of the Q bands (521, 553, 591 and 647 nm) and the development of a Q band at around 687 nm, when compared to a non-exposed H_2TPP film (Figure 6 inset).

Both "red-shifts" (H_2TPP solution → non-exposed H_2TPP film → NO_2 exposed H_2TPP film) are attributed to the aggregation state of molecules in the film. These findings are partially endorsed by similar published research from Tonezzer and co-workers[6] investigated H_2TPP and CoTPP films produced by spin coating and vacuum evaporated techniques. These systems were studied in different alcohol atmospheres (methanol, ethanol and propanol) and their effect on optical absorbance was analyzed. Also, Richardson and co-workers[9] have achieved a fast response time for calixarene/porphyrin LB films which can be potentially applied as NO_2 organic sensing material.

Figure 7 shows the difference between two films formed by LB and LS, indicating different intensities in absorbance and thereby reflecting on the thickness of each formed film, by considering that absorption intensity is proportional to thickness – Beer's law.

3.3. Molecular orientation of phorphyrin in LB and LS films

The orientation of H_2TPP molecules in LB and LS films (two layers) was estimated by measuring the UV-vis absorption dichroism (Figure 8) at the Soret band from porphyrin (433 nm) and the polarized UV-vis spectra data are summarized in the Table 2. The orientation angles normal to the film and the dipping direction, respectively θ, ϕ were calculated[18] by the following Equations 4 and 5:
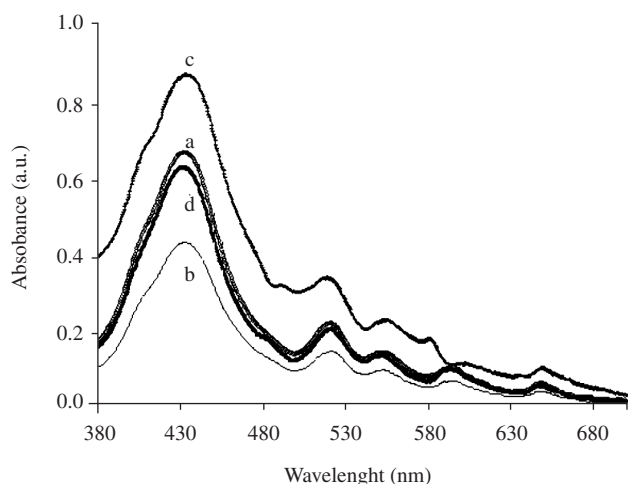
$$\cos^2\theta = [D_0 - (1 + D_0 \sin^2\beta) D\beta] / [(1 - 2\sin^2\beta) D\beta - (1 + D\beta \sin^2\beta) D_0] \quad (4)$$

$$\sin^2\theta \cos^2\phi = (D_0 - \cos^2\theta)/(1+D_0) \quad (5)$$

Considering the uncertainty of $\pm 5°$ that comes from the polarized UV–vis method[2], the results indicated that the macrocycle of H_2TPP in LB film was tilted by an angle of $51 \pm 5°$ and in the LS film was tilted by an angle of $36 \pm 5°$ (Figure 9). Both values are in good agreement

Table 2. Polarized UV-vis spectra results calculated at $\lambda = 433$ nm for H$_2$TPP LB and LS films.

Incident angle	Dichroic ratios	LB film	LS film
	Av	0.659	0.135
$\beta = 0°$	Ah	0.425	0.097
	D$_0$	1.551	1.392
	Av	0.905	0.238
$\beta = 45°$	Ah	0.619	0.126
	D$_{45}$	1.462	1.889
Results	Equations 2 and 3	LB film	LS film
	cos$^2\theta$	0.746	0.914
	θ	51.4	35.1
	ϕ	30.3	17.1

Figure 8. Results of absorption dichroism measurement for two layers on quartz substrate of a H$_2$TPP LB film, pH 5. a) A$_{v0}$, b) A$_{h0}$, c) A$_v\theta$, and d) A$_h\theta$.
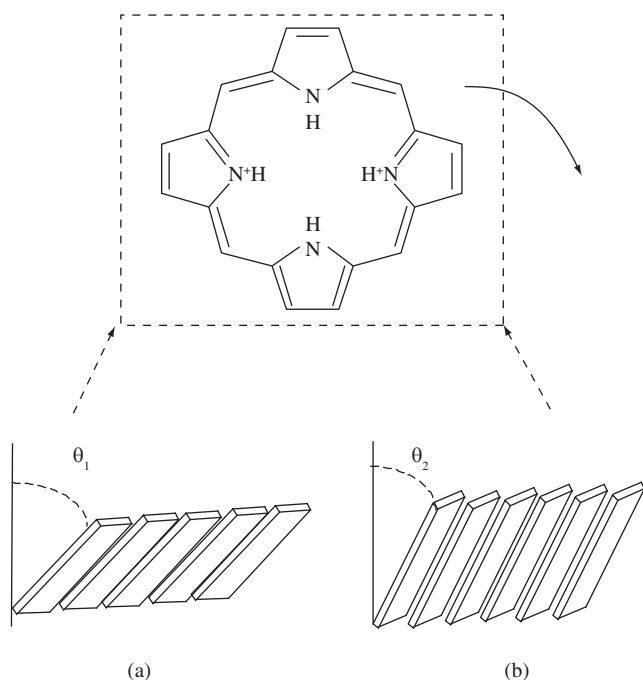
Figure 9. Schematic illustration of possible arrangements of H$_2$TPP in: a) LB film and in b) LS film.

with the literature[2]. Hence, these results confirmed that the H$_2$TPP molecules did not form flat LB and LS films and but the trend of a tilted molecular organization as preferential average conformation where the angle is dependent on the deposition method used. A more in-depth investigation is required to fully understand such behavior as far as the molecular film is transferred onto the substrate and its dynamic thermodynamic stabilization process.

The structures of the monolayers before and after being transferred onto solid substrates may differ due to the different environments. That is, the tilt angle of the porphyrin macrocycle normal to the substrates is slightly larger than that normal to air/liquid interface, arising from the elimination of the surface pressure[19]. According to the playing-card model, porphyrin rings arrange parallel one to another, and the corresponding transition moments in adjacent rings are also parallel in the supramolecular structure formed at the air/water interface. For this kind of alignment of the transition moments, the exciton model developed by Kasha and others[20] predicts that the shift or splitting of absorption bands in weakly coupled electronic systems is caused by the interaction of localized transition dipole moments[11]. This theory explains that for free-base porphyrins that have two orthogonal transition moments, there are two angles α_1 and α_2, related to the center-center line between the adjacent rings. If $\alpha_2 = 90°$ then α_1 corresponds to the orientation angle of the ring θ related to the normal angle of substrate and the results for $\theta = \alpha_1 < 54.7°$ is the red shifted of absorption band, indicating that J aggregates are formed[3,7,21].

4. Conclusions

The response of 5, 10, 15, 20-tetraphenylporphyrin to the presence of NO$_2$ gas in diluted solutions and in Langmuir-Blodgett and Langmuir-Schaefer films was verified by UV-visible spectroscopy based upon the shift of Soret and Q bands. A relatively simple and inexpensive gas reactor was built for gas detection. The exposure of LB porphyrin films deposited onto glass slides to NO$_2$ has performed as an active chemical detector with about 7000 ppm gas concentration. Additionally, the UV-vis dichroism absorption results associated with the spectroscopy characterization have given evidence of the tilt angle of the macrocycle deposited on the substrate. H$_2$TPP LB film was tilted by an angle of $51 \pm 5°$ and the LS film was tilted by an angle of $36 \pm 5°$ indicating the formation of a preferential organization of the molecular films depending on the deposition method. In summary, the developed H$_2$TPP molecular films indicated an opportunity of potential use for NO$_2$ chemsensor applications.

Acknowledgements

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