

FREE-BASE CARBOXYPHENYL PORPHYRIN/TiO₂ COMPOSITE POROUS FILMS FOR THE OPTICAL DETECTION OF NO₂

José M^a Pedrosa^{*†}, Tânia Lopes-Costa[†], María G. Guillén[†], Belén Suárez[†], Javier Roales[†]

^{*} Corresponding author. E-mail: jmpedpoy@upo.es

[†]Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, Carretera Utrera km 1, 41013 Sevilla, Spain

Key words: NO₂ gas sensor, porphyrin, microstructured TiO₂ thin films, GAPVD.

Summary: *In this work we have studied the anchoring effect of three different free-base carboxyphenyl porphyrins to TiO₂ microstructured columnar films and its influence on NO₂ sensing. Stability and aggregation have been studied through UV-vis and infrared spectroscopy. Binding to TiO₂ thin films were corroborated by FTIR. When exposed to NO₂, thin films suffer important changes in their UV-vis spectra, which demonstrate that the porphyrins have an extraordinary potential to be used as sensitive sensors for the detection of NO₂, with fast and intense responses. Moreover, concentration-dependent responses has been found when composite films are exposed to low concentrations of NO₂ confirming their applicability for calibration purposes.*

1 INTRODUCTION

Porphyrins are a family of compounds with chemical and physical properties that make them interesting for new technologies such as solar cells [1], photodynamic therapies [2] or gas sensors [3]. They have shown to be promising for the creation of sensing devices of low price and ease of use that could be applied to electronic nose technologies. In particular, and based on the photophysical properties of porphyrins, their potential use for the construction of optical devices for gas sensing has attracted great attention [3–5].

Nitrogen dioxide, given its high toxicity and participation as a precursor in the formation of other contaminants such as tropospheric ozone, fine particulate matter (PM_{2.5}) and acid rain, is of environmental concern especially in urban locations, where it is formed in relatively high concentrations from vehicle motor exhausts and other sources of combustion of fossil fuels. The interaction between NO₂ and some free-base porphyrins is well documented in the literature, producing strong changes in the absorption spectrum that can be easily monitored [4,6,7]. Usually, porphyrin films have been made by Langmuir-Blodgett, spin coating or casting techniques, and these films have shown good sensing capabilities. Great efforts have been made to improve the sensitivity of porphyrin films to NO₂, either by

modifying the technique of deposition or combining the sensing material with host molecules, with outstanding results [8]. However, films made by these techniques are sometimes unstable given the little interaction between porphyrin and substrate, which leads to a short or mid-term unusability caused by porphyrin aggregation. Strong π - π interactions between porphyrins favor the formation of molecular aggregates that have shown to be detrimental for gas sensing purposes [9].

Anchoring of porphyrin molecules to TiO₂ by adding carboxylic acid groups to their structure has given great results in terms of film fabrication and its applicability [10] due to chemical binding to TiO₂ leads to more stable films than the simple deposition onto glass. However, films made from colloidal suspensions of this material are usually thick and opaque, and hence not appropriate for optical measurement. Glancing angle physical deposition (GAPVD) films feature TiO₂ microstructured columns that make possible the covalent binding of carboxylic porphyrins to their surface, adding stability to the film properties. Moreover, they are transparent enough to be used for optical sensing and highly porous, allowing easy diffusion of gas molecules through their inner structure [11].

Besides the influence of the porphyrin-substrate interaction on the film stability, porphyrin aggregation is influenced by the molecular structure of the dye. It is known that bulky substituents can reduce aggregation by preventing porphyrin contact [7,12], and the position itself of the peripheral groups may determine different states and types of aggregation [9] [13].

Here we evaluate the anchoring effect on free-base carboxyphenyl porphyrin films using TiO₂ microstructured columns as host matrix and its influence on NO₂ sensing. In this case, we have chosen unmetalated porphyrins which are known to be good candidates for the detection of NO₂ [4,7,9,14]. Three different free-base porphyrins have been used for this purpose: 5-(4-carboxyphenyl)10,15,20-triphenyl-21*H*,23*H*-porphyrin (MCTPP, Figure 1A), 5,10,15,20-tetrakis(4-carboxyphenyl)-21*H*,23*H*-porphyrin (*p*-TCPP, Figure 1B) and 5,10,15,20-tetrakis(3-carboxyphenyl)-21*H*,23*H*-porphyrin (*m*-TCPP, Figure 1C). The aggregation and stability of the composite films regarding the different binding geometries have been studied through UV-vis and infrared spectroscopy. Finally, the sensing capabilities towards NO₂ have been investigated by analyzing the responses of the composite films upon their exposure to different concentrations of the toxic gas.

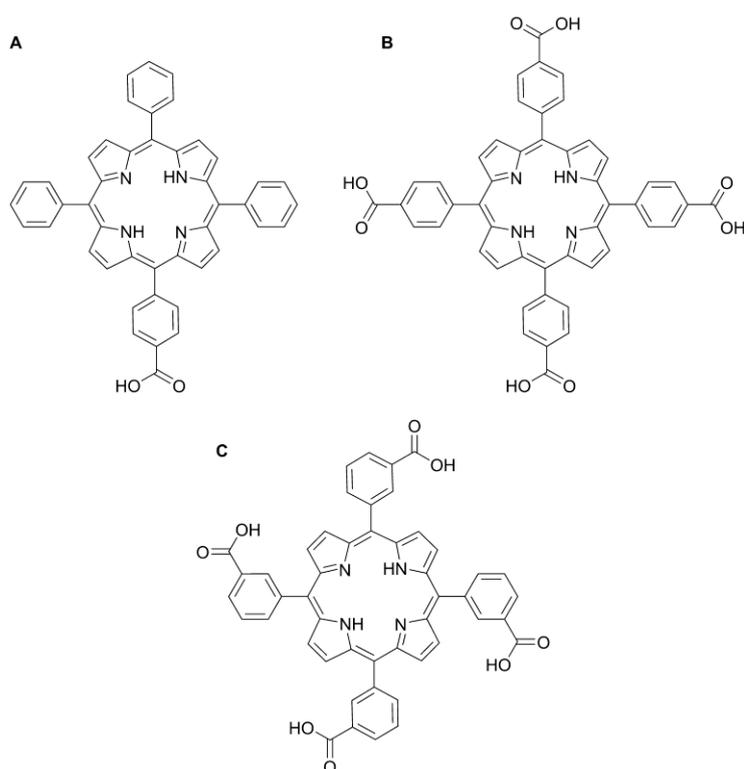


Figure 1: Molecular structures of (A) 5-(4-carboxyphenyl)10,15,20-triphenyl-21*H*,23*H*-porphyrin (MCTPP), (B) 5,10,15,20-tetrakis(4-carboxyphenyl)-21*H*,23*H*-porphyrin (*p*-TCPP), and (C) 5,10,15,20-tetrakis(3-carboxyphenyl)-21*H*,23*H*-porphyrin (*m*-TCPP).

2 RESULTS AND DISCUSSION

2.1. Composite porphyrin/TiO₂ films characterization

Figure 2 shows UV-vis solution spectra of MCTPP, *p*-TCPP and *m*-TCPP showed their monomeric forms with Soret bands peaking at 414, 415 and 415 nm, respectively. Once bound to TiO₂, each porphyrin experienced different changes in their spectra. The shape of the Soret band revealed the contribution of two peaks, indicating the presence of, at least, two species in the films, the monomeric and the H aggregated forms of the porphyrins. The spectrum of *m*-TCPP bound to TiO₂ showed much more similarity to that obtained from its solution.

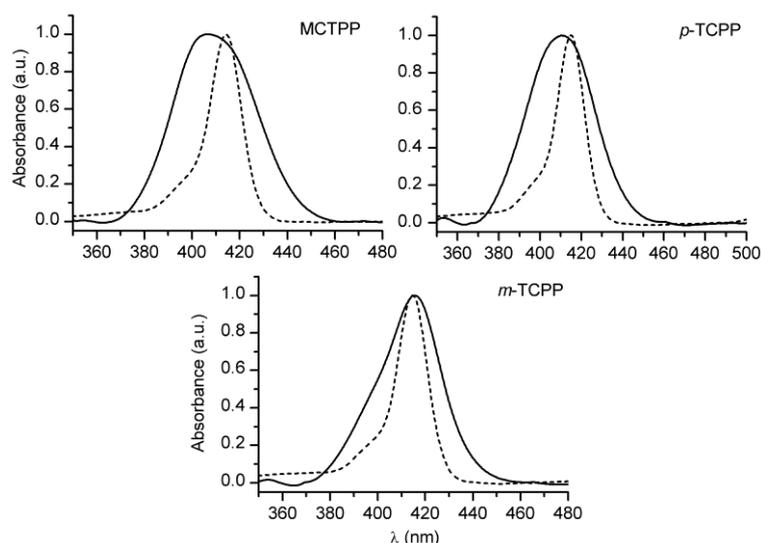


Figure 2: Normalized UV-vis absorption spectra of MCTPP, *p*-TCPP and *m*-TCPP bound to TiO₂ (solid line) and in MeOH solution (dashed line).

The *m*-TCPP films remained stable after seven months indicating that composite films made with this porphyrin are highly stable as it is shown in Figure 3. On the contrary, MCTPP and *p*-TCPP films spectra showed a flat line without any trace of their respective Soret bands after seven months, may be attributed to the extended formation of porphyrin clusters leading to an uncolored film.

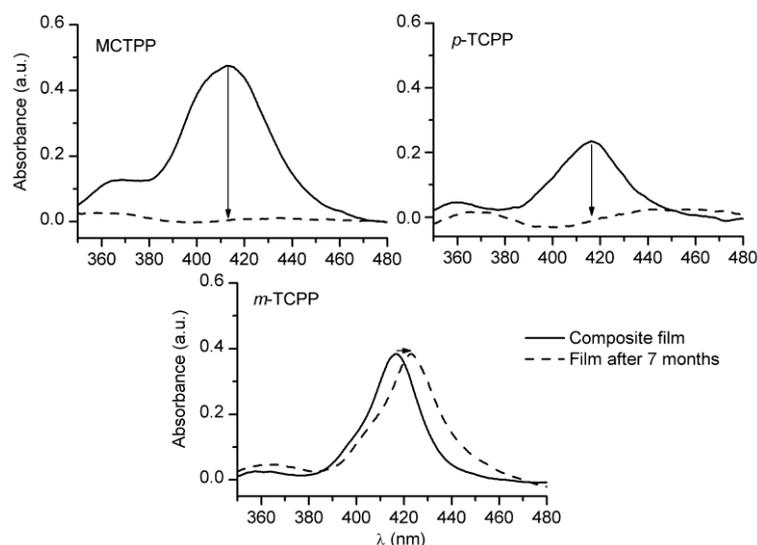


Figure 3: UV-vis absorption spectra of MCTPP/TiO₂, *p*-TCPP/TiO₂ and *m*-TCPP/TiO₂ composite films after preparation (solid line) and seven months later (dashed line).

The differences in the aggregation state and stability of the porphyrins in film can be explained through their different binding to the TiO₂ matrix. MCTPP would be anchored by its only carboxylic group, which leads to a flexible union between porphyrin and TiO₂ that would allow dye molecules to tilt and rotate, facilitating contact between porphyrin rings and, thus, their aggregation. In the case of *p*-TCPP, its four carboxylic groups are located in the *para* position of the phenyl groups, leading to a planar structure. With this arrangement, the binding through four points is almost impossible, being more plausible the presence of one or

two anchoring points. Therefore, *p*-TCPP would also be bound with its tetrapyrrolic ring normal to the TiO₂ surface, allowing face to face interaction and subsequent molecular aggregation. The structure of *m*-TCPP is similar to *p*-TCPP, but in this case the four carboxylic groups are situated in the *meta* position of the phenyl groups, hence orientated perpendicular to the plane of the molecule. This configuration allows the porphyrin to anchor by four points to the TiO₂ matrix while lying flat to the surface, resulting in a fixed position for each porphyrin that hinders aggregation and provides higher stability to the film than in the case of MCTPP or *p*-TCPP.

Further confirmation regarding binding modes of porphyrin molecules to TiO₂ and their influence on aggregation was obtained by the analysis of their specular reflectance FT-IR spectra shown in Figure 4, attending to bands characteristic of ν (C=O) and the ν (C-O) stretches of the carboxylic acid groups.

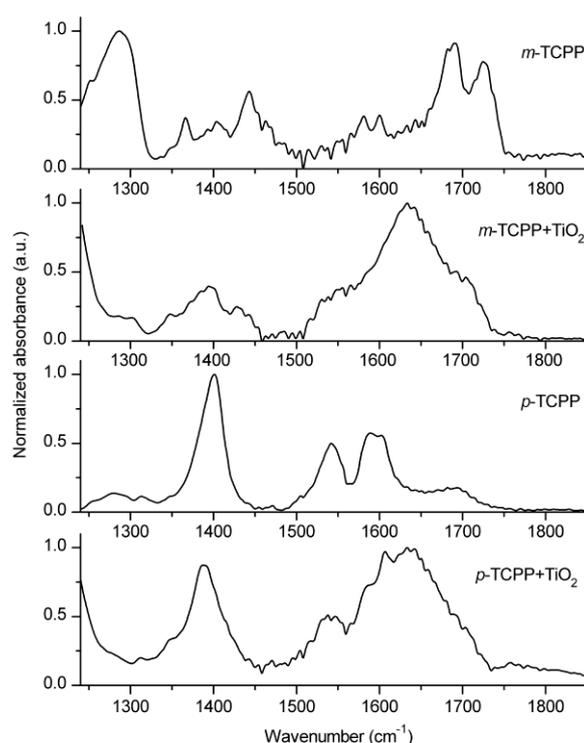


Figure 4. Specular reflectance FT-IR spectra of *m*-TCPP and *p*-TCPP neat (by casting on silicon substrates) and bound to TiO₂.

Chemical binding of carboxylic acids to TiO₂ colloidal films has been associated with the disappearance of the bands corresponding to the ν (C=O) and ν (C-O) stretching modes, and the appearance of strong and broad bands at ~ 1400 cm⁻¹ and ~ 1550 cm⁻¹, characteristic of the symmetric and asymmetric ν (CO₂⁻) stretches respectively. [10] These spectral changes have been found to be compatible with chelating and/or bidentate binding modes of the carboxylate groups on the TiO₂ surface

2.2. NO₂ detection

MCTPP/TiO₂, *p*-TCPP/TiO₂ and *m*-TCPP/TiO₂ composite films were exposed to 500 ppm NO₂ to assess their sensing performance. The exposure of the films to the toxic gas was

carried out in a purpose-built gas chamber previously flushed with dry N₂ to ensure an inert internal atmosphere, thus preventing the contamination the samples. In Figure 5, spectra of porphyrins films before and after exposure to NO₂ are shown. The typical Soret band of the porphyrins disappeared, appearing a new band around 435 nm which is consistent with a charge transfer process in the form of oxidation documented by other authors using different free-base porphyrins [4,7,9,15], given that porphyrins are electron-rich systems and NO₂ is a strong oxidizing agent.

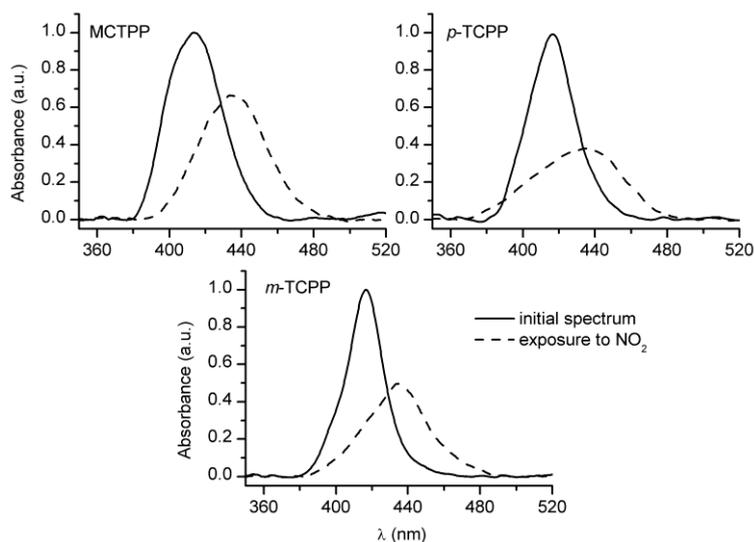


Figure 5. Pre-exposure (solid line) and exposure (dashed line) spectra of MCTPP/TiO₂, p-TCPP/TiO₂ and m-TCPP/TiO₂ composite films upon exposure to 500 ppm NO₂.

The magnitude of the spectral changes was high in all cases, but recovery of the samples was only partially achieved after heating the samples under a N₂ stream, which makes them good candidates for single-use NO₂ sensors. Other recovery strategies are a subject of further research.

The speed of response was analyzed by monitoring the absorbance at one of the wavelengths of maximum change during the exposure of the composite films to 500 ppm NO₂. All porphyrins featured fast changes with similar response shapes. To quantify the speed of response, we calculated the time taken for the absorbance to reach 50% of its maximum value (t_{50}), with 31, 30, and 33 sec respectively for MCTPP/TiO₂, p-TCPP/TiO₂ and m-TCPP/TiO₂ composite films, confirming the fast response of all of them.

There is no clear evidence that anchoring geometries have a strong influence on the sensing capabilities. However, the less aggregated state and much better stability over time achieved by m-TCPP once bound to TiO₂ suggests this as the best candidate among our set of porphyrins to be used as NO₂ sensor as it is shown in Figure 6. The exposure to decreasing concentrations of NO₂ led to a decreasing Absorbance change, indicating a concentration-dependent behavior of the system.

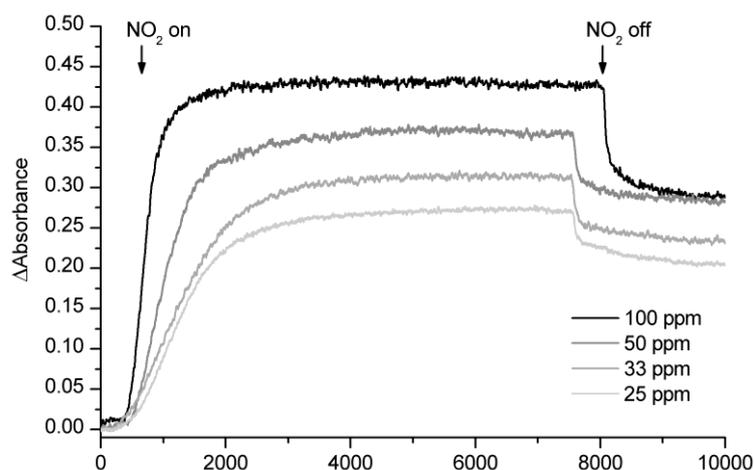


Figure 6. Kinetics of the exposure of *m*-TCPP/TiO₂ composite films to 25, 33, 50 and 100 ppm NO₂ at a wavelength of 442 nm.

Characterization of the concentration dependence fitted quite well with a Langmuir adsorption isotherm model [16] which is very interesting for calibration purposes.

3 CONCLUSION

Composite films based on microstructured columnar TiO₂ films and free-base porphyrins have been prepared in order to analyze their gas-sensing capabilities towards NO₂. These films, owing to their ease of preparation and high stability, are a convenient alternative to those obtained by more complicated and time-consuming techniques, such as Langmuir-Blodgett, which often produce films of unsatisfactory stability and are unsuitable for commercial purposes.

UV-vis spectra of MCTPP/TiO₂, *p*-TCPP/TiO₂ and *m*-TCPP/TiO₂ composite films have revealed that *m*-TCPP/TiO₂ films are the most stable, showing less aggregation than the other porphyrins and peaking at the same wavelength as its monomeric solution.

IR spectroscopy has shown that *m*-TCPP is bound to TiO₂ through its four carboxylic acid groups, while *p*-TCPP is anchored by only one or two of these groups. MCTPP, given its structure, can only be bound to the TiO₂ by one carboxylic acid. As a result of this, *p*-TCPP and MCTPP flexible binding allows them to tilt and rotate producing aggregates. This effect is greatly reduced by the more fixed anchoring of *m*-TCPP, which enhances the stability of its films.

The exposure of MCTPP/TiO₂, *p*-TCPP/TiO₂ and *m*-TCPP/TiO₂ composite films to NO₂ has resulted in important changes in their UV-vis spectra, revealing good sensing capabilities that were similar in all cases, with fast and intense responses. Given that no important differences have been found in the responses of the different porphyrins upon their exposure to NO₂, *m*-TCPP would be the best candidate for the fabrication of NO₂ sensors, given its higher stability.

Finally, the exposure of *m*-TCPP/TiO₂ composite films to low concentrations of NO₂ has shown concentration-dependent responses, increasing their magnitude and speed of response as the concentration of the gas increased, hence confirming the potential of *m*-TCPP as NO₂ sensor.

3 REFERENCES

- [1] Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science*, **334**, 629–34, 2011.
- [2] Dougherty, T. J.; Gomer, C. J.; Henderson, B. W.; Jori, G.; Kessel, D.; Korbelik, M.; Moan, J.; Peng, Q. *Photodynamic therapy. J. Natl. Cancer Inst.* **90**, 889–905, 1998.
- [3] Rakow, N. A.; Suslick, K. S. A colorimetric sensor array for odour visualization. *Nature* **406**, 710–3, 2000.
- [4] Dooling, C. M.; Worsfold, O.; Richardson, T. H.; Tregonning, R.; Vysotsky, M. O.; Hunter, C. A.; Kato, K.; Kaneko, F.; Shinbo, K. *J. Mater. Chem.* **11**, 392–398, 2001.
- [5] Suslick, K. S.; Rakow, N. A.; Sen, A. *Tetrahedron* **60**, 11133–11138, 2004.
- [6] Pedrosa, J. M.; Dooling, C. M.; Richardson, T. H.; Hyde, R. K.; Hunter, C. A.; Martin, M. T.; Camacho, L. *J. Mater. Chem.* **12**, 2659–2664, 2002.
- [7] Gulino, A.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I.; Fragalà, I. *Chem. Mater.* **16**, 1838–1840, 2004.
- [8] De Miguel, G.; Martín-Romero, M.; Pedrosa, J. M.; Muñoz, E.; Pérez-Morales, M.; Richardson, T. H.; Camacho, L. *J. Mater. Chem.* **17**, 2914–2920, 2007.
- [9] Pedrosa, J. M.; Dooling, C. M.; Richardson, T. H.; Hyde, R. K.; Hunter, C. A.; Martín, M. T.; Camacho, L. *Langmuir*, **18**, 7594–7601, 2002.
- [10] Rochford, J.; Chu, D.; Hagfeldt, A.; Galoppini, E. *J. Am. Chem. Soc.* **129**, 4655–4665, 2007.
- [11] Roales, J.; Pedrosa, J. M.; Castillero, P.; Cano, M.; Richardson, T. H.; Barranco, A.; González-Elípe, A. R. *ACS Appl. Mater. Interfaces* **4**, 5147–5154, 2012.
- [12] Gulino, A.; Bazzano, S.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I.; Fragalà, I. *Chem. Mater.* **17**, 521–526, 2005.
- [13] Roales, J.; Pedrosa, J. M.; Cano, M.; Guillén, M. G.; Lopes-Costa, T.; Castillero, P.; Barranco, A.; Gonzalez-Elípe, A. R. *RSC Adv.* **4**, 1974–1981, 2014.
- [14] Dunbar, A. D. F.; Richardson, T. H.; Hutchinson, J.; Hunter, C. A. *Sensors Actuators, B Chem.* **128**, 468–481, 2008.
- [15] Richardson, T. H.; Dooling, C. M.; Jones, L. T.; Brook, R. A. *Adv. Colloid Interface Sci.* **116**, 81–96, 2005.
- [16] Langmuir, I. *J. Am. Chem. Soc.* **40**, 1361–1403, 1918.