DETECCIÓN DE COMPUESTOS ORGÁNICOS VOLÁTILES Y GASES TÓXICOS MEDIANTE SENSORES ÓPTICOS BASADOS EN PELÍCULAS MICROESTRUCTURADAS DE PORFIRINAS

DETECTION OF VOLATILE ORGANIC COMPOUNDS AND TOXIC GASES BY OPTICAL SENSORS BASED ON MICROSTRUCTURED PORPHYRIN FILMS

TESIS DOCTORAL

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DETECCIÓN DE COMPUESTOS ORGÁNICOS VOLÁTILES Y GASES TÓXICOS MEDIANTE SENSORES ÓPTICOS BASADOS EN PELÍCULAS MICROESTRUCTURADAS DE PORFIRINAS

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OBJETIVOS

Los trabajos desarrollados en esta memoria quedan englobados en la línea de investigación dedicada al diseño y desarrollo de dispositivos sensores de gases y compuestos orgánicos volátiles para el análisis y control de calidad de productos alimenticios y calidad medioambiental del aire, llevada a cabo por el grupo "Química Física de Fases Condensadas e Interfases" (FQM319). Los objetivos generales que se han establecido para esta tesis son:

a) Preparar películas delgadas de porfirinas mediante diferentes métodos con el fin de optimizar la estructura interna de las mismas en la aplicación para la que son diseñadas.

b) Estudiar, mediante diferentes técnicas de caracterización, la organización molecular de las películas formadas.

c) Analizar las capacidades sensoras de las películas preparadas mediante su exposición a gases tóxicos y compuestos orgánicos volátiles.

d) Explorar nuevas formas de representación de los cambios producidos en las películas de porfirinas tras su exposición a gases tóxicos y compuestos orgánicos volátiles, que mejoren la detección y discriminación de los mismos.
The work described in this report belongs to the research line dedicated to the design and development of gas-sensing devices for the analysis and quality control of food products and environmental quality of air, carried out by the group “Química Física de Fases Condensadas e Interfases” (FQM319). The main goals of this research were as follows:

a) To prepare porphyrin thin films by different methods in order to optimize their inner structure for the application that they are designed for.

b) To study, through different characterization techniques, the molecular organization of the prepared films.

c) To analyze the sensing capabilities of the prepared films through their exposure to toxic gases and volatile organic compounds

d) To explore new methodologies for the representation of the changes produced to the porphyrins after their exposure to toxic gases and volatile organic compounds, that improve their detection and discrimination.
En la presente memoria se estudia la preparación de películas de porfirinas y su aplicación como material sensor para la detección óptica de compuestos orgánicos volátiles (COVs) y gases tóxicos. El resumen de esta memoria se ha organizado según los capítulos en los que se estructura esta tesis.

En el Capítulo 1, constituido por la Introducción general, se ha profundizado en aspectos que pueden ser relevantes y que en los capítulos correspondientes a los resultados obtenidos se han tratado de una forma más superficial. De esta forma, la Introducción general queda dividida en cuatro bloques principales. En el primero de ellos se hace una exposición de la importancia de los gases tóxicos y COVs, tanto desde el punto de vista de sus riesgos ambientales como de las tecnologías basadas en la detección de los últimos. En el segundo bloque se explica el interés de la detección de gases y se exponen los principales métodos existentes para ello, con principal atención a los sistemas electrónicos de olfato y a los sistemas ópticos basados en colorantes. En tercer lugar se describen las propiedades químicas y ópticas de las porfirinas y las aplicaciones tecnológicas que se basan en ellas. Por último, se describen los principales métodos de deposición de porfirinas sobre soportes sólidos y las principales técnicas de caracterización de películas delgadas.

El Capítulo 2, o Experimental, describe con profundidad el montaje y los aspectos técnicos de los diferentes métodos utilizados a lo largo de esta memoria, complementando la información de este tipo presente en los posteriores capítulos.

El resto de los capítulos que forman esta memoria contienen los resultados obtenidos durante el desarrollo experimental de la tesis y se resumen a continuación:

Capítulo 3. Se han preparado películas mixtas de Langmuir-Blodgett a partir de la porfirina EHO y el calixareno C8A a una proporción molar de 3:2 para controlar la agregación de EHO, y se ha discutido la importancia de la ausencia de agregación a raíz de nuevos resultados experimentales. También se han estudiado las diferentes respuestas a NO2 de las películas mixtas de EHO:C8A con respecto a su espesor. Por último, se han analizado las propiedades de la superficie de las películas mixtas mediante microscopia de fuerza atómica (AFM) y se han relacionado con sus cinéticas de exposición al gas tóxico.

Capítulo 4. Se ha utilizado una porfirina carboxílica no metálica y 11 de sus derivados metálicos para la detección óptica de COVs. Para esto, se ha usado películas microcolumnares de TiO2 como matriz contenedora de las porfirinas, y el enlace químico entre las porfirinas y el TiO2 se ha confirmado mediante espectroscopia FT-IR. Además, se ha investigado la influencia del anclaje en la agregación y orientación de las porfirinas. Por último, se han analizado las respuestas ópticas del conjunto de porfirinas frente a un total de 12 COVs individuales, y la
**Resumen**

La magnitud de los cambios espectrales se ha representado en forma de patrones de reconocimiento en color que permiten la distinción de cada analito.

_Capítulo 5._ Se han preparado películas mixtas de porfirina y TiO₂ columnar microestructurado utilizando dos tipos de carboxifenilporfirinas metálicas, una con los grupos carboxílicos en posición *meta* y otra con estos en posición *para*, y se han comparado sus propiedades sensoras con respecto al tipo de anclaje y el estado de agregación. Para esto, el enlace químico entre las porfirinas y el TiO₂ se ha confirmado mediante espectroscopia FT-IR. También se ha investigado la influencia de este anclaje en la orientación y en el estado de agregación de las porfirinas. Se han analizado las respuestas ópticas de los dos tipos de porfirinas frente a seis COVs, individualmente, para comprobar si la diferente posición de los sustituyentes periféricos juega un papel importante en las propiedades sensoras de gases de estas moléculas.

_Capítulo 6._ Se ha evaluado el efecto del anclaje y su influencia en la detección de NO₂ usando tres tipos de carboxifenilporfirinas no metálicas con columnas microestructuradas de TiO₂ como matriz. La agregación y estabilidad de las películas mixtas con respecto a las diferentes geometrías de anclaje se han estudiado por espectroscopia UV-vis y FT-IR. Por último, se han investigado las capacidades sensoras de NO₂ mediante el análisis de las respuestas de las películas mixtas frente a diferentes concentraciones del gas tóxico.

_Capítulo 7._ Se ha utilizado una porfirina tripodal para la detección de aminas, y se ha comparado esta con la porfirina individual que la forma para analizar la influencia de la estructura ramificada en la agregación molecular y sus propiedades sensoras. Se han utilizado cinco aminas, tres de ellas lineales (unidimensionales) de creciente longitud, una plana (bidimensional) y una ramificada (tridimensional), para comprobar si la geometría de la porfirina tripodal facilita la detección selectiva de aminas con respecto a su forma y tamaño.
SUMMARY

In this report, the preparation of porphyrin films and their application as sensor material for the optical detection of volatile organic compounds (VOCs) and toxic gases is studied. The summary of this report is organized according to the chapters that form this thesis.

In Chapter 1, constituted by the General introduction, the aspects that may be relevant and have been treated superficially in subsequent chapters, have been analyzed in detail. In this way, the General introduction is divided in four main blocks. In the first one, the importance of toxic gases and VOCs is explained, taking into account both the environmental risks associated to them and the technologies based in the detection of the latter. In the second block, the interest in the detection of gases is explained, and the main methods available for this purpose are shown, with special attention to electronic olfactory devices and dye-based optical systems. In third place, the chemical and optical properties of porphyrins and the technological applications derived from them are described. Finally, the main methods for the deposition of porphyrins onto solid substrates and the main techniques for the characterization of thin films are explained.

In Chapter 2, or Experimental, it is described the set-up and technical details of the different methods used in this report, complementing the information available in subsequent chapters.

The rest of the chapters forming this report, which include the results obtained during the PhD investigation, are summarized as follows:

Chapter 3. Mixed Langmuir-Blodgett films containing EHO porphyrin and C8A calixarene at a molar ratio of 3:2 have been prepared in order to control the EHO aggregation, and the importance of the absence of aggregation has been further discussed in the light of recent experimental results. The different responses of the EHO:C8A mixed films to NO\textsubscript{2} regarding the film thickness have also been studied. Finally, the properties of the surface of the mixed films have been analyzed through atomic force microscopy (AFM) analysis and related to their kinetics of exposure to the toxic gas.

Chapter 4. The carboxylic acid derivatives of a free–base porphyrin and 10 of its metal derivatives have been used for optical gas sensing of VOCs. For this purpose, microstructured columnar TiO\textsubscript{2} thin films have been used as hosts for the porphyrins and the chemical binding between the porphyrin and the TiO\textsubscript{2} has been confirmed through infrared spectroscopy. Also, the influence of this binding on the porphyrin aggregation and orientation has been investigated. The optical responses of the set of porphyrins to a total of 12 individual VOCs have been analyzed, and the magnitude of the spectral changes has been represented as color image patterns with spectral
Summary

resolution which allows selective recognition for each analyte.

Chapter 5. Composite films made of microstructured columnar TiO\textsubscript{2} and two
different metallic carboxyphenyl porphyrins featuring their carboxylic groups in
meta and para positions, respectively, have been prepared, and their sensing
properties regarding both the anchoring to the TiO\textsubscript{2} and the molecule aggregation are
compared. For this purpose, the chemical binding between the porphyrin and the
TiO\textsubscript{2} has been confirmed through infrared spectroscopy. Besides, the influence of this
binding on the aggregation and orientation of porphyrin molecules has been
investigated. The optical responses of the two porphyrins to a total of 6 individual
VOCs have been analyzed to test if the different peripheral substituent position plays
an important role on the gas-sensing properties of these molecules.

Chapter 6. The anchoring effect on three different free-base carboxyphenyl
porphyrin films using TiO\textsubscript{2} microstructured columns as host matrix and its influence
on NO\textsubscript{2} sensing has been assessed. The aggregation and stability of the composite
films regarding the different binding geometries have been studied through UV-vis
and FT-IR spectroscopy. Finally, the sensing capabilities towards NO\textsubscript{2} have been
investigated by analyzing the responses of the composite films upon their exposure
to different concentrations of the toxic gas.

Chapter 7. A tripodal porphyrin has been used to detect amines through UV-vis
spectroscopy, and this has been compared to its single unit to account for the
influence of the branched structure on molecular aggregation and sensing
capabilities. In order to test if the geometry of the tripodal porphyrin facilitates the
selective detection of amines regarding their size and shape, a total of five amines
have been used, being three of them linear (one-dimensional) with increasing length,
one planar (two-dimensional) and one with a branched structure (three-dimensional).
INTRODUCCIÓN

En esta memoria se persigue optimizar las metodologías existentes para la detección de compuestos orgánicos volátiles (COVs) y gases tóxicos, y proponer y desarrollar nuevas opciones que resulten en un avance en este campo de investigación. El interés por los COVs y gases tóxicos parte no sólo de su importancia como contaminantes, sino también de las aplicaciones tecnológicas que se pueden desarrollar a partir de su detección. El uso de sensores ópticos basados en películas de porfirinas se propone como una alternativa a los métodos de detección más utilizados y disponibles comercialmente, con potencial para la creación de dispositivos de fácil uso y bajo coste. A continuación se hace una introducción a los aspectos más relevantes para contextualizar este estudio.

1. Compuestos orgánicos volátiles y gases tóxicos

Multitud de COVs y gases tóxicos, emitidos tanto de forma natural como por procesos antrópicos, están presentes en nuestro entorno formando parte del aire que respiramos. Su participación en un gran número de procesos y su influencia sobre la salud de los humanos y otros seres vivos hace que exista un interés creciente por controlar su presencia en determinados ambientes. Más allá de sus riesgos ambientales, la presencia de ciertos COVs o de combinaciones de ellos puede utilizarse como indicador de enfermedades, procesos de descomposición o determinadas características organolépticas, por lo que las tecnologías basadas en su detección están en continuo desarrollo.

1.1 Riesgos ambientales

Ciertos COVs y gases tóxicos existentes de forma natural desempeñan un papel importante en el mantenimiento de nuestro ecosistema. El CO$_2$, por ejemplo, es necesario para que sea posible la fotosíntesis y por lo tanto la producción de oxígeno, esencial para nuestra supervivencia y la de tantos otros seres vivos. Otro ejemplo es el NO$_2$, cuya existencia previene la acumulación de ozono en las capas más bajas de la atmósfera, letal para los humanos. Sin embargo, la llegada de la revolución industrial a finales del s. XIX alteró el balance natural de estos gases tóxicos en el ambiente, de forma que a principios del s. XX ciertas ciudades muy industrializadas presentaban una niebla espesa ahora conocida como smog. Esto se unió a la llegada del automóvil como nueva fuente de contaminación.\textsuperscript{1}

Uno de los gases tóxicos que se originan a partir de la combustión de
combustibles fósiles es el NO\textsubscript{2} que puede dañar gravemente el sistema respiratorio humano,\textsuperscript{2} contribuye a la formación de lluvia ácida y tiene un papel importante en la formación de ozono troposférico.\textsuperscript{3,4} Debido a estos factores, y principalmente por su alta toxicidad, el NO\textsubscript{2} es controlado frecuentemente por las autoridades ambientales especialmente en grandes ciudades, donde se forma en grandes concentraciones como parte de los gases de combustión de los automóviles.

Los COVs, que pueden proceder tanto de fuentes naturales como de procesos antropogénicos, son otro grupo importante de contaminantes atmosféricos, dada su extensa presencia en diversos ambientes y su relación con problemas de salud a largo plazo.\textsuperscript{5} Las mayores fuentes de emisión de COVs son algunos tipos de industrias, como las refinerías de petróleo y petroquímicas, y los automóviles, siendo estos últimos los responsables de un 35\% de las emisiones totales.\textsuperscript{6,7} Sin embargo, al contrario que en el caso del NO\textsubscript{2}, los COVs también son emitidos en el interior de hogares y lugares de trabajo a partir de productos combustibles, materiales de construcción, pinturas, barnices, disolventes o adhesivos, entre otros.\textsuperscript{8–10} Esto hace que las concentraciones de COVs dentro de los hogares y lugares de trabajo pueda ser incluso mayor que en el exterior. Teniendo en cuenta que una gran parte de la población pasa hasta un 80\% de su tiempo en su residencia o en su lugar de trabajo,\textsuperscript{11,12} la presencia de COVs en estos lugares es potencialmente peligrosa para la salud.\textsuperscript{13} De hecho, mientras que exposiciones cortas a ciertos COVs no se consideran dañinas para la salud, exposiciones prolongadas pueden producir efectos mutagénicos y cancerígenos.\textsuperscript{14} Tal es el caso, por ejemplo, de compuestos aromáticos como la anilina, de probada toxicidad, y cuya presencia debe ser controlada en ciertos ambientes industriales.\textsuperscript{15}

1.2 Otras aplicaciones basadas en la detección de COVs

La participación de los COVs en múltiples procesos naturales hace que su presencia o ausencia pueda usarse como indicador de diversos tipos. Por ejemplo, los sistemas de olfato electrónico, también llamados narices electrónicas, han mostrado potencial para la caracterización de muestras alimentarias sin la necesidad de utilizar paneles de cata formados por expertos. Estos sistemas analizan el perfil organoléptico de la muestra analizada, formado en gran parte por COVs, y proporcionan un perfil de respuesta que identifica y clasifica cada muestra.\textsuperscript{16}

Un grupo importante dentro de los COVs, las aminas, son utilizadas como indicadores de diversos procesos. Algunas aminas biogénicas, como la histamina, putrescina o cadaverina, aparecen como productos metabólicos bacterianos de la descomposición de comida, principalmente pescado y carne, lo que hace posible que se usen como indicador de la frescura o estado de conservación de estos alimentos.\textsuperscript{17,18} También se pueden detectar algunas enfermedades gracias a la presencia de concentraciones inusuales de ciertas aminas, producidas en este caso
por infecciones bacterianas, como es el caso de la vaginosis 19.

2. Detección de gases

La necesidad de detectar la presencia de algunos gases, bien sea para evitar sus efectos tóxicos o para el análisis de muestras alimentarias o biológicas, ha hecho que se desarrollen distintas metodologías adaptadas a cada caso concreto. Técnicas como la cromatografía de gases (GC) y de líquidos (LC) o la espectrometría de masas (MS) se usan desde hace años para identificar y cuantificar diversos compuestos gaseosos con buenos resultados. Esto a menudo incluye el uso de captadores, pasivos o activos, que atrapan los gases de interés en una disolución captadora o un adsorbente sólido, y del que posteriormente se extraen los compuestos contenidos en su interior para su análisis mediante una de las técnicas anteriores. Sin embargo, estos procedimientos tienen inconvenientes como la destrucción de las muestras analizadas, tiempos de análisis relativamente lentos y un largo procesado de datos, aparte del elevado precio de los equipos de análisis.20,21

Los sistemas electrónicos de olfato, también llamados narices electrónicas, se han utilizado como alternativa a las técnicas anteriores, basando su funcionamiento en un conjunto de diferentes sensores con la capacidad de proporcionar una respuesta global ante un determinado gas o mezcla de gases.22,23 Estos sistemas, al contrario que la cromatografía, no implican la separación de muestras complejas en cada uno de sus componentes, reduciendo el tiempo necesario para el análisis y evitando la destrucción de la muestra. Los sensores que forman parte de estos equipos están compuestos habitualmente de óxidos metálicos semiconductores24 y su funcionamiento se basa en la medición de la variación de su conductividad eléctrica al interaccionar con el gas que se pretende detectar. Estos sensores han mostrado buenos resultados en la discriminación de analitos de diferentes grupos funcionales, pero la distinción de compuestos dentro de una misma clase química sigue siendo una tarea pendiente.25 Además, estos materiales no han proporcionado buenos resultados para la detección de especies con potencial para unirse a metales, entre las que se encuentran muchos compuestos tóxicos. Por este motivo, la detección de aminas, fosfinas y tieoles mediante este tipo de sensores no se ha conseguido de forma satisfactoria.26 Otros inconvenientes de este tipo de sensores son su elevada temperatura de funcionamiento (400-600 °C) y su inestabilidad frente a cambios de humedad, lo que puede dificultar la comparación de muestras de diferentes características.

Durante las últimas décadas se ha investigado sobre la posibilidad de utilizar sensores basados en sistemas ópticos de forma similar a los sistemas electrónicos de olfato comerciales. Estos sistemas se fundamentan en la detección de gases mediante la monitorización óptica de un colorante cuyo espectro se ve modificado en presencia...
Introducción
del gas en cuestión. La elección del colorante a utilizar viene determinada por los
gases que se quieren detectar. En la literatura científica se pueden encontrar
numerosos estudios hechos con porfirinas, ftalocianinas, indicadores ácido-base y otros colorantes. Dada la especificidad de las interacciones entre
colorante y gas, ciertos autores han realizado estudios con conjuntos de sensores o
arrays compuestos por varios colorantes, de forma que puedan dar una respuesta selectiva frente a mezclas de gases.

En el caso de esta tesis, se han utilizando distintos derivados de porfirinas como
material sensor, dadas sus propiedades fotoquímicas y fotofísicas que se detallan a
continuación, que las hacen candidatos ideales para la detección de una gran variedad de analitos.

3. Porfirinas

3.1 Propiedades químicas y ópticas

Las porfirinas son la familia de pigmentos altamente coloreados responsable del
verde de nuestros bosques y del rojo de nuestra sangre. Todas las porfirinas están
constituidas por el mismo núcleo, llamado porfina, que al mismo tiempo sería la
porfirina más sencilla. Este núcleo está formado por cuatro pirroles unidos por
grupos metino y recibe comúnmente el nombre de anillo tetrapirrólico (Figura 1). Es
posible la modificación de este anillo tanto en su periferia, incorporando
sustituyentes laterales de distintos tipos, como en su interior, reemplazando los
atamos de hidrógeno centrales por un átomo metálico, unido por enlaces de
coordinación. Se forman así múltiples combinaciones que darían lugar a las
incontables porfirinas existentes de forma natural o que se pueden obtener a través
de síntesis. Los ejemplos más conocidos de porfirinas son las hemo, acomplejadas
con hierro y presentes en la hemoglobina, y las clorinas, que contienen magnesio en
su núcleo y forman parte de las clorofilas.

Figura 1. Estructura molecular del anillo tetrapirrólico, base de todas las porfirinas.
Capítulo 1

El espectro típico de absorción de una porfirina meso-sustituida no metálica en su forma monomérica es tal y como se muestra en la Figura 2. Este espectro siempre está compuesto por una intensa banda de absorción alrededor de 390-425 nm, conocida como banda Soret, y de dos a cuatro bandas de menor intensidad localizadas a mayores longitudes de onda (alrededor de 480-700 nm), llamadas bandas Q. El número, posición e intensidad de estas bandas depende de los sustituyentes que incluya la porfirina y de la presencia o ausencia de un átomo metálico en su núcleo. Por ejemplo, una porfirina no metálica presenta cuatro bandas Q, mientras que la presencia de un átomo metálico reduce estas bandas a dos, debido al cambio de simetría de la molécula.

![Espectro de absorción de una disolución de porfirina no metálica. Se muestra una ampliación de las bandas Q entre 485 y 675 nm.](image)

3.2 Aplicaciones tecnológicas

Las propiedades de las porfirinas las hacen muy atractivas para el desarrollo de nuevas aplicaciones tecnológicas. Su intensa coloración hace que en los últimos años se haya investigado su potencial para la creación de celdas solares basadas en pigmentos. Gracias a esta misma característica es posible su utilización como fotosensibilizador en terapias fotodinámicas para el tratamiento del cáncer.

Un campo de investigación que recientemente ha mostrado mucho interés por las propiedades de las porfirinas es el de la detección de gases. El rico sistema de electrones π presente en el macrociclo de las porfirinas puede verse modificado por la presencia de ciertos gases, modificando de forma notable su espectro de absorción y sirviendo como base para crear dispositivos sensores de gases. Además, las excelentes propiedades ópticas de los derivados de porfirinas, con un espectro de absorción muy intenso y localizado dentro del visible, hace que sean fácilmente monitorizables con espectrofotómetros UV-vis de bajo coste.

La capacidad de las porfirinas para interaccionar con diversos gases depende de
factores como el metal contenido en el centro del anillo tetrapirrólico o sus sustituyentes periféricos. Durante las últimas décadas se ha estudiado ampliamente la química orgánica de las porfirinas, existiendo numerosas rutas de síntesis para la introducción de un amplio rango de sustituyentes en sus posiciones periféricas y de un gran número de metales en su núcleo. De esta forma, las propiedades sensoras de estas moléculas pueden ser diseñadas de forma precisa.

Existen numerosos estudios realizados en las últimas décadas en los que se utilizan porfirinas para la detección de gases. En concreto, la interacción de porfirinas no metálicas con gases como el NO₂ está bien documentada en la literatura, y la detección de COVs ha mostrado resultados prometedores, principalmente usando porfirinas metálicas. La gran cantidad de porfirinas existentes y sus variadas propiedades sensoras hace que sean candidatas ideales para la creación de conjuntos de sensores o arrays que puedan dar una respuesta cruzada frente a muestras complejas de gases, de forma selectiva y a bajo coste.

4. Deposición de porfirinas sobre soportes sólidos

La utilización de porfirinas como material activo para la fabricación de sensores de gases implica la utilización de algún tipo de soporte sólido que las contenga. La interacción gas-sólido es un fenómeno de tipo superficial, por lo que es fundamental que la disposición del material sensor garantice una alta relación superficie/volumen. La deposición en forma de películas delgadas y el uso de materiales altamente porosos asegura esta propiedad.

Por otra parte, la presencia de interacciones π–π entre porfirinas puede causar la agregación de estas, provocando el ensanchamiento, desplazamiento e incluso la división de las bandas propias de su espectro con respecto al estado monomérico en disolución. Esta agregación puede ser perjudicial para aplicaciones sensoras, ya que la interacción con las moléculas gaseosas incidentes se ve dificultada de forma importante por el apilamiento de los macrociclos. Por lo tanto, es necesario utilizar una técnica de deposición apropiada para controlar la formación de agregados, de forma que se obtengan unas buenas cualidades sensoras.

4.1 Métodos de deposición de porfirinas

4.1.1 Spin-coating

Después de la técnica de casting, consistente en depositar una o varias gotas de una disolución que contiene el material de interés sobre un soporte sólido y esperar a que se evapore el disolvente, la metodología de spin-coating es quizás la más sencilla para preparar películas delgadas. En esta técnica se hace girar un soporte, típicamente de vidrio, tras haberle añadido en el centro un cierto volumen de una
disolución con el compuesto que formará la película. De esta forma, la disolución se extiende por la superficie del vidrio hasta ser expulsada de éste por la fuerza centrífuga generada. Una vez seca, y si hay suficiente afinidad entre el soporte y la disolución, queda una fina película recubriendo el soporte. Dada la sencillez del procedimiento y el bajo coste del equipo necesario (spin coater), es una técnica fácil de implementar para producir películas de diversos materiales.

Sin embargo, en el caso de las porfirinas, las fuertes interacciones intermoleculares existentes entre los anillos tetrapirrólicos a menudo promueven la formación de agregados que, como ya se ha dicho, puede disminuir la habilidad sensora de estas películas. La deposición de porfirinas por spin-coating produce películas desordenadas y, a menos que exista algún tipo de interacción fuerte entre el soporte y la porfirina, sin ningún tipo de anclaje que evite la posterior agregación de las moléculas. Una de las opciones más utilizadas para evitar esta agregación es la adición de grandes grupos periféricos a la porfirina, de forma que éstas queden separadas. El inconveniente de esta opción es que la presencia de grupos periféricos puede reducir las capacidades sensoras de las porfirinas. Alternativamente, la creación de estructuras de multiporfirinas puede prevenir la agregación de estas al evitar su contacto por repulsión estérica, siendo evitada por completo la agregación entre las subunidades de porfirinas. Ciertas de estas multiporfirinas, como las tripodales sintetizadas por Pinto et al., han demostrado tener propiedades similares a su unidad monomérica, permitiendo el acceso de pequeñas moléculas gaseosas al interior de su estructura tridimensional y con el potencial de reducir la agregación en películas con respecto a su correspondiente porfirina monomérica.

4.1.2 Películas de Langmuir-Blodgett

La técnica de Langmuir-Blodgett (LB) permite construir y ensamblar películas simples sobre soportes sólidos a partir de monocapas preparadas previamente en la interfase aire-agua mediante la técnica de Langmuir. La formación de estas monocapas se basa en la insolubilidad de las moléculas que las forman y en su carácter anfílico. La preparación se lleva a cabo añadiendo una cantidad de moléculas anfílicas sobre la superficie del agua, tras lo que se comprime la monocapa hasta conseguir un empaquetamiento máximo de las moléculas, de forma que se llega a una fase de estado sólido. Tras esto, la deposición en sólido se realiza mediante la colocación de un soporte sólido perpendicular a la interfase aire-agua cubierta por las monocapa que se va a transferir, de forma que mediante la inmersión y/o emersión de dicho soporte las moléculas se van depositando sobre el soporte sólido. Durante esta transferencia se compensa la pérdida de moléculas en la interfase mediante la compresión de la monocapa, para así mantener constante la presión superficial y el estado de empaquetamiento de las moléculas.

La preparación de películas de LB permite un alto control sobre el ordenamiento
molecular, pudiéndose conocer detalles como la orientación y el número de moléculas existentes. Gracias a esto, es una técnica muy utilizada para la creación de películas sensoras. Sin embargo, no todas las moléculas tienen la capacidad de crear este tipo de película por no poseer un carácter suficientemente anfílico. En el caso de las porfirinas, esta propiedad puede conseguirse mediante la adición de ciertos grupos periféricos, que al mismo tiempo ayudan a reducir la agregación ya comentada entre estas moléculas gracias a la separación de sus núcleos. Otra forma de mejorar las películas es la utilización de moléculas que actúen como hospedadoras de las porfirinas. Es el caso de los calixarenes, moléculas con forma de cálib, que al alojar las porfirinas en su interior reducen de forma significativa las posibilidades de que se agreguen. Al mismo tiempo aumentan la rugosidad de las películas, incrementando la relación superficie/volumen y mejorando sus capacidades sensoras.

4.1.3 Anclaje a matrices porosas

En la búsqueda de soportes para la creación de sensores de gases, algunos autores han utilizado ciertos medios porosos, como geles de sílice o silicatos modificados orgánicamente (ormosiles), a modo de soporte para contener diferentes pigmentos, entre ellos porfirinas. Mientras tanto, investigadores en el campo de las celdas solares han estado sensibilizando TiO$_2$ con colorantes orgánicos como fotorreceptores, y algunos de ellos se han centrado en las porfirinas por su participación en la fotosíntesis. Como resultado, se ha estudiado el anclaje al TiO$_2$ de grupos funcionales como salicilato, ácido sulfónico, ácido fosfónico y ácido carboxílico, siendo éste último uno de los grupos más utilizados. Sin embargo, las películas de TiO$_2$ preparadas para celdas solares suelen ser gruesas y opacas, lo que las hace inapropiadas para la detección óptica de gases mediante espectroscopía UV-vis.

Una forma de evitar estos inconvenientes es mediante la preparación de las películas de TiO$_2$ por deposición física de vapor en ángulo rasante (GAPVD). Estos materiales se caracterizan por una microestructura columnar con poros abiertos y de gran tamaño que permiten la fácil entrada de moléculas a su interior, lo que no sólo permite la incorporación de porfirinas a la película sino que facilita la difusión de gases a través de ella. Además, su alta porosidad y escaso grosor hacen que tengan un grado de transparencia muy alto, permitiendo medidas ópticas de transmisión. Por otra parte, la posibilidad de un anclaje químico con las porfirinas mediante la inclusión de uno o varios de los grupos funcionales anteriormente indicados hace prever una alta estabilidad de las películas y una escasa agregación de las moléculas de porfirina, lo que resultaría en una probable mejora de las capacidades sensoras con respecto a otros métodos de preparación de películas. Todo esto hace que estas películas microestructuradas sean muy buenos candidatos para la fabricación de
Capítulo 1

sensores basados en porfirinas.

4.2 Técnicas de caracterización de películas

Una vez preparada la película sensora es necesario conocer detalles de su estructura y organización para poder predecir o explicar su comportamiento frente a la exposición a gases. Para esto se pueden utilizar diversas técnicas de caracterización como: espectroscopia de absorción UV-vis; espectroscopia infrarroja con transformada de Fourier (FT-IR); microscopias electrónica de barrido (SEM), de fuerza atómica (AFM), electrónica de transmisión (TEM), de efecto túnel (STM) y de ángulo Brewster (BAM); elipsometría o difracción de rayos X.

La técnica más utilizada en esta memoria ha sido la espectroscopia de absorción UV-vis, mediante la que se han monitorizado los cambios ocurridos en los espectros de las películas de porfirina tras la exposición a los respectivos gases estudiados. También se ha utilizado esta técnica para conocer el estado de agregación de las porfirinas en las películas, gracias a los cambios que sufre su espectro cuando ocurre este fenómeno.

Mediante la espectroscopia FT-IR se ha caracterizado la unión de porfirinas carboxílicas a las matrices columnares de TiO$_2$. De esta forma se ha comprobado el enlace entre porfirina y TiO$_2$, y además ha sido posible predecir la geometría del anclaje, fundamental para comprender los distintos comportamientos de las diferentes porfirinas carboxílicas.

Por último, la microscopia SEM se ha utilizado para caracterizar las matrices columnares de TiO$_2$, dando información sobre su estructura, grosor y porosidad, y la microscopia AFM ha servido para obtener información fundamental para comprender las diferencias entre películas LB preparadas con diferentes componentes.

Bibliografía

Introducción

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EXPERIMENTAL

1. Técnicas de formación de películas

1.1 Spin-coating

Las películas preparadas por spin-coating se fabricaron utilizando un spin coater Laurell WS-400B-6NPP Lite. Este equipo consiste básicamente en una plataforma, donde se coloca el soporte de la película, en nuestro caso vidrio, que gira a una determinada velocidad (Figura 1). Previamente al comienzo de la rotación, sobre el soporte se deposita una pequeña cantidad de una disolución que contiene las moléculas que formarán la película. Para evitar que el soporte salga despedido de la plataforma al girar, una bomba de vacío le aplica succión desde un orificio en la plataforma, manteniéndolo unido a esta. Gracias a la fuerza centrífuga producida por el giro, la disolución se extiende por toda la superficie del soporte y el sobrante sale despedido hacia fuera de él. De esta forma queda una película delgada cuyo grosor no depende de la cantidad de disolución añadida, sino de su concentración y afinidad por el soporte. Las películas se depositaron sobre portaobjetos de vidrio (Menzel-Glaser microscope slides) cortados a una medida de aproximadamente 4 cm², utilizando disoluciones de las correspondientes porfirinas en cloroformo. El equipo fue programado en tres fases para girar 5 s a 500 rpm, seguidos de 2 s a 2000 rpm y una fase final de 30 s a 4000 rpm. Después de esto, se calentaron las películas a 100 ºC para desorber los restos de disolvente que pudieran haber quedado atrapados en su interior.
Figura 1. Interior del Spin coater Laurell WS-400B-6NPP Lite. Las muestras quedan fijadas sobre el círculo negro en el centro de la imagen mediante la aplicación de vacío. La plataforma central gira a la velocidad deseada durante la preparación de las películas.

1.2 Langmuir-Blodgett

Para la fabricación de películas LB se utilizó una balanza de Langmuir NIMA de tipo rectangular. Este instrumento consta de una cuba de material plástico e inerte (Teflón), donde queda alojado el líquido que constituirá la subfase (en este caso agua ultrapura a pH 5.7 y 21 °C), y sobre el que se deposita la disolución que contiene el material que formará la película; dos barreras móviles que cumplen con la función de comprimir la monocapa; y un sistema Wilhelmy de medición de la presión superficial (Figura 2). Este sistema está constituido por una lámina de papel de cromatografía parcialmente sumergida en la subfase y conectada a una microbalanza electrónica de alta sensibilidad. La presencia de la monocapa sobre la subfase acuosa modifica la tensión superficial con respecto a la subfase pura, y esta variación es precisamente la presión superficial que registra el sistema Wilhelmy. La velocidad de compresión utilizada para la creación de las monocapas osciló entre 10-20 Å molécula⁻¹ min⁻¹.
La transferencia de monocapas a soportes sólidos se realizó mediante un brazo mecánico acoplado a la balanza que se mueve perpendicularly mente a la monocapa. Este brazo sostiene el soporte, y por inmersión/emersión de este en la subfase a través de la monocapa se consigue la transferencia. La velocidad de transferencia fue de \( 5 \text{ mm min}^{-1} \) para las películas mixtas de EHO:C8A y \( 1000 \text{ mm min}^{-1} \) en el caso de las películas de EHO pura, para las que se usó una técnica de deposición ultra rápida \(^1\). Las películas se transfirieron sobre soportes de vidrio para los análisis UV-vis y sobre soportes de silicio para el análisis por AFM. Ambos tipos de soporte fueron hidrofobizados previamente con 1,1,1,3,3,3-hexametildisilazano para favorecer la transferencia.

1.3 Películas mixtas de porfirina/TiO\(_2\)

La preparación de películas microestructuradas de TiO\(_2\) se llevó a cabo mediante GAPVD. Esta técnica consiste en evaporar TiO en estado sólido mediante su bombardeo con un haz de electrones de alta energía, en condiciones de vacío de aproximadamente \( 1 \times 10^{-4} \) Torr de O\(_2\), para obtener películas de TiO\(_2\). Los soportes se colocan en posición vertical de un portamuestras hecho a medida para este fin, de forma que al condensarse el vapor en su superficie se crea una película delgada de TiO\(_2\). La estructura resultante es de tipo columnar, con una inclinación determinada por el ángulo que forma el punto de evaporación con la superficie del soporte. Las películas se prepararon sobre soportes de vidrio para los análisis UV-vis y sobre soportes de silicio para su análisis por microscopía FESEM.

La incorporación de porfirinas a las películas de TiO\(_2\) se llevó a cabo por inmersión de estas en una disolución con las porfirinas correspondientes durante una

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**Figura 2.** Balanza de Langmuir NIMA de tipo rectangular. En la imagen se distingue la cuba de Teflón ocupando el centro, las dos barreras móviles a derecha e izquierda y el sistema Wilhelmy de medición de la presión superficial en el centro de la parte superior.
o dos horas, según el caso, a temperatura ambiente (20 ºC). Una vez realizada la infiltración, las películas se enjuagaron con el mismo disolvente empleado en la disolución anterior para eliminar las porfirinas adsorbidas pero no ancladas. Por último, se secaron las películas a temperatura ambiente bajo una corriente de N₂ o aire.

2. Técnicas de caracterización de películas

2.1 Espectroscopia UV-vis

La espectroscopía UV-vis se ha utilizado para caracterizar las películas y para analizar sus propiedades sensoras. Los espectros se obtuvieron en un especetrofotómetro World Precision Instruments SpectroMate u Ocean Optics USB4000, según el caso. Ambos espectrofotómetros están equipados con fibras ópticas que permiten llevar el haz de luz proveniente de la lámpara hacia el lugar donde se encuentra la muestra y recoger la porción de luz que la atraviesa para llevarla al detector. De esta forma se puede medir el espectro de absorción UV-vis de muestras colocadas en distintos portamuestras, lo que es fundamental durante la fase de exposición a gases, para la que se requiere la introducción de las muestras en una cámara de gases. Los espectros en disolución se obtuvieron utilizando cubetas de cuarzo Hellma de paso óptico 1 cm.

2.2 Espectroscopia FT-IR

Para las medidas de infrarrojo se utilizó un espectrómetro Jasco FT/IR-6200 utilizando el método de reflectancia especular. Esta técnica permite el análisis de películas delgadas y proporcionó información fundamental para conocer el tipo de anclaje en las películas mixtas de porfirina/TiO₂. Todos los espectros se obtuvieron usando 500 escaneos a una resolución de 4 cm⁻¹.

2.3 Microscopia AFM

Las medidas de AFM para analizar la topografía de las películas de EHO y EHO:C8A se realizaron usando un microscopio AFM NanoScope IIIa Multimode con el software NanoScope III. Esta es una técnica de medida superficial que se basa en la interacción de una punta con la superficie de la muestra, y permite su análisis con resolución nanométrica o incluso atómica. Las imágenes se obtuvieron usando el modo tapping en aire, en el que la punta se hace vibrar sobre la superficie. Para el post-procesado y el análisis de rugosidad de las imágenes se utilizó el software WSxM.

2.4 Microscopia SEM

La microestructura de las películas de TiO₂ preparadas por GAPVD se analizó por microscopía electrónica de barrido de emisión de campo (FESEM) utilizando un microscopio Hitachi S5200. Las secciones transversales se obtuvieron haciendo un corte a
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los soportes de silicio. Esta técnica permite obtener una imagen detallada de la superficie y el perfil de la microestructura columnar de las películas de TiO$_2$, de forma que se pueden definir algunas de sus características más importantes, como las dimensiones de su estructura o su porosidad.

3. Sistema de exposición a gases

Para hacer posible la exposición de las muestras a los gases analizados se utilizaron dos sistemas de exposición a gases fabricados expresamente para este objetivo, de características equivalentes. Estos sistemas consisten en una cámara de acero inoxidable construida al efecto con una entrada y una salida de gases, a través de los cuales se inunda la cámara del gas en cuestión; conectores para dos cables de fibra óptica, encargados de suministrar luz a la muestra a partir de la lámpara y de llevar la porción transmitida hasta el detector del espectrofotómetro; y un sistema termoeléctrico Peltier para el control de la temperatura (Figura 3). En los dos casos, el sistema se completa con un cuadro de mezcla de gases, que permite obtener de forma precisa la concentración deseada del gas. Este cuadro está formado por dos controladores de flujo móscicos Bronkhorst F-201FV o Tylan FC-260 y una serie de conductos y válvulas que permiten la realización de mezclas gaseosas tanto a partir de gases embotellados como en combinación de estos con volátiles en estado líquido.

La preparación de las mezclas con NO$_2$ se realizó a partir de botellas conteniendo NO$_2$ en N$_2$ a una concentración de 5 o 500 ppm, suministrados por BOC (Reino Unido) o Air Liquide (España). La obtención de concentraciones intermedias se obtuvo por dilución de la corriente conteniendo NO$_2$ con otra proveniente de una
segunda botella de N\textsubscript{2} puro, de los mismos proveedores, mediante la modificación de los caudales respectivos utilizando los controladores de flujo másico.

Para la obtención de vapores de COVs se utilizó un montaje diferente. En este, la corriente obtenida a la salida de una botella de N\textsubscript{2} se dividió para distribuirla entre los dos controladores de flujo másico. Una de las corrientes, a la salida de su respectivo controlador, se hizo pasar a través del COV en estado líquido o de una mezcla de este con dodecano, en aquellos casos en los que fue necesario reducir de forma importante la concentración del COV. En ambos casos se utilizó un baño termostático para controlar la temperatura de la disolución y por lo tanto la presión de vapor del COV. Una vez obtenida una corriente de N\textsubscript{2} portadora de vapores de COVs, esta se diluyó con la otra corriente proveniente del segundo controlador de flujo másico, obteniéndose así la concentración deseada del COV de forma precisa. La concentración final se calculó a través de la presión de vapor del COV en cuestión a la temperatura correspondiente y del factor de dilución con N\textsubscript{2}.

La exposición a gases se realizó en todos los casos a temperatura ambiente (~21 °C). En las fases de recuperación, las muestras se calentaron a temperaturas elevadas (entre 80 y 110 °C) mediante el sistema termoelecétrico Peltier bajo una corriente de N\textsubscript{2} puro, para favorecer la desorción de las moléculas de gas de la película sensora y el retorno a su estado inicial.

Durante todo el proceso (pre-exposición, exposición y recuperación), el espectro UV-vis de las muestras fue monitorizado mediante los cables de fibra óptica conectados a un espectrofotómetro, haciendo posible tanto la obtención de espectros completos como las cinéticas de exposición o recuperación a determinadas longitudes de onda.

4. Materiales y reactivos

La mayoría de los materiales y reactivos que se han utilizado en los diferentes experimentos descritos en esta memoria fueron adquiridos a través de las firmas comerciales que se detallan en los capítulos correspondientes. En los casos de productos sintetizados no comerciales se da la referencia bibliográfica donde se describe su síntesis.

5. Tratamiento de datos

Los datos obtenidos a partir de los diferentes equipos científicos utilizados se trataron con los programas Origin Pro, en el caso de los espectros UV-vis y FT-IR, y WSxM\textsuperscript{2}, para el análisis de imágenes de AFM, que a su vez se utilizaron para la creación de las figuras presentadas en esta memoria. Las estructuras moleculares fueron creadas con el programa ChemDraw.
Bibliografía


1. Introduction

Porphyrrins and phthalocyanines have been widely investigated because of their photophysical and photochemical properties, which are based on a rich π-electron system [1] that make them able to interact with gases [2]. During the last few years, the possibility of depositing this kind of materials as thin films on solid substrates, allowing the construction of optical devices for gas sensing, has attracted great attention [3-5]. Fossil fuels combustion is known to produce a wide variety of toxic gases. One of these dangerous compounds is NO₂, which damages seriously the respiratory system [6], contributes to acid rain and takes part in the formation of tropospheric ozone [7,8]. To reduce these health risks for the environment and humans, more accurate sensors are necessary.

Porphyrrins are interesting as gas sensors because their highly conjugated π-electron system yield significant changes in their UV-visible absorption spectrum during the exposure to various compounds. In particular, NO₂ gas exhibit a strong interaction with free base porphyrins producing a shift in the energies of the conjugated π-electrons in the macrocycle and therefore changing the absorption spectrum [9].

Previous studies [10,11] have shown that the absorbance spectrum of Langmuir-Blodgett (LB) films of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO, Fig. 1(a)) is very sensitive to low concentrations of NO2 gas. In particular, heterogeneous and porous films have been found to enhance the gas sensing properties of EHO [10] and other similar porphyrins [12]. The thickness dependence of the NO2 gas response in EHO LB films was studied in a previous work, and the number of layers was found to influence the kinetics of the response to the toxic gas [11]. On the other hand, the interaction of the porphyrin with the NO₂ gas molecules can be influenced by the possible molecular aggregation existing between the macrocycles when they are deposited on solid substrates. A close molecular packing can even prevent the interaction between gas and porphyrin [3].

Finally, it has been demonstrated that the preparation of a mixed Langmuir film
containing EHO and p-tert-butylcalix[8]arene (C8A, Fig. 1 (b)) reduces the aggregation of the porphyrin molecules on water, as compared to that for the pure EHO. The C8A molecules act as matrix for the porphyrin, leading to very stable and flexible films. The organization of the EHO molecules is influenced by the C8A matrix, which diminishes partially the porphyrin aggregation through the formation of a more balanced hydrophilic/hydrophobic environment at the air water interface [13,14]. The effect of the new organization for the EHO molecules in mixed films with C8A, has been clearly manifested by the enhancement of the response time (faster), reproducibility (higher), sensitivity (higher) and temperature response (wide range, of interest for industrial applications) during exposure to NO\textsubscript{2}, in comparison with those results previously obtained for the more aggregated pure EHO film [13,14].

![Fig. 1. Molecular structures of EHO (a) and C8A (b).](image)

In the present work, mixed LB films containing EHO and C8A at a molar ratio of 3:2 have been prepared in order to control the EHO aggregation, and the importance of the absence of aggregation has been further discussed in the light of recent experimental results. The different responses of the EHO:C8A mixed films to NO\textsubscript{2} regarding the film thickness have also been studied. Finally, the properties of the surface of the mixed films have been analyzed through atomic force microscopy (AFM) analysis and related to their kinetics of exposure to the toxic gas.

### 2. Experimental details

#### 2.1 Materials

The porphyrin EHO was obtained according to the synthesis described elsewhere [10]. The calix[8]arene C8A was synthesized following the method of Davis et al. [15,16]. Both compounds (Fig. 1) were used without further purification. Pure
chloroform (Merck) was used as spreading solvent and used as received. Ultrapure water was obtained from a Millipore Direct-Q system (>18 MΩ cm) and used throughout.

2.2 Methods

Mixed monolayers of the C8A:EHO at a molar ratio of 3:2 were prepared on pure water at pH 5.7 and 21 ºC. This ratio was found to be the optimum in previous works [13,14] and will be maintained in all the subsequent experiments. After evaporation of the organic solvent, the mixed film was compressed or expanded using a movable barrier on a Nima rectangular trough provided with a filter paper Wilhelmy plate [17] with a compression velocity of 10–20 Å molecule⁻¹ min⁻¹, facilitating the recording of surface pressure-area (p-A) isotherms.

The monolayers were transferred onto hydrophobic glass substrates, for the UV-visible analysis, and onto hydrophobic silicon substrates, for the AFM analysis. Glass substrates were previously cleaned several times with CHCl₃ and rinsed with pure water. Silicon substrates were cleaned in a Sohxlet extractor with acetone for 4 h and dried in air. A silanising agent, 1,1,1,3,3,3-hexamethyldisilazane, was used to render glass and silicon substrates hydrophobic by immersing in the solution for 24 hours.

The C8A:EHO multilayers were assembled by sequential monolayer transfer, that is, immersion and withdrawal of the substrate through the interface covered with the mixed film. The number of monolayers transferred is indicated in each sample, where the “excursion” means immersion and subsequent withdrawal process, i.e., two monolayers. The speed of transfer process was 5 mm min⁻¹ of a mixed film compressed at 25 mN m⁻¹. The transfer ratio, t, was close to unity for all transfer processes. LB films of pure EHO were prepared using the ultra-fast deposition technique (1000 mm min⁻¹) [10], which leads to better transfer ratios than conventional LB deposition speed.

A purpose-built gas testing chamber [10] was used to assess the gas-sensitivity optical properties of C8A:EHO LB films. The gas stream (NO₂ obtained at 5 ppm in dry nitrogen, BOC, Guildford, UK, and dry nitrogen as recovery gas) was directed into the gas testing chamber that held the mixed layer samples. A WPI Spectromate optical fiber spectrophotometer incorporating a multichannel photodiode array detector was used to record visible absorption spectra of the sample over the wavelength range 350–850 nm. Data were collected every 1.5 s during the exposure/recovery cycles. The exposure to the toxic gas occurred at 293 K and the recovery phase (dry nitrogen only) at 350 K.

Atomic force microscopy measurements were performed using a NanoScope IIIa Multimode AFM with NanoScope III software to analyze the topography of the solid films. Images were taken in tapping imaging mode in air [18]. The post-processing
Optimization of mixed LB films of porphyrin/calixarene for optical gas sensing

and roughness analysis to the images was performed using WSxM software [19].

3. Results and discussion

The temporal evolution of the UV-visible absorbance spectrum of a mixed C8A:EHO LB film (5 excursions) during the exposure to 5 ppm NO₂ gas stream is shown in Fig. 2. Before the exposure to NO₂, the porphyrin spectrum is observed with the Soret band appearing at 427 nm. As the NO₂ exposure starts, the Soret band becomes weaker, with the simultaneous growth of two bands around 470 and 708 nm. These spectral changes could indicate protonation of the porphyrin ring or oxidation [3,10]. Given that porphyrins are electron-rich systems and NO₂ is a strong oxidizing agent, a charge transfer process is the most probable mechanism for such spectral changes [20,21].

Fig. 2. Temporal evolution (t) of the UV-visible absorbance spectrum of a mixed C8A : EHO 3 : 2 LB film (5 excursions) during the exposure to 5 ppm NO₂ gas stream (time interval = 1.5 s).

In a previous study [13], the mixed C8A:EHO LB system has been found to enhance the sensing response with respect to the pure EHO. The results showed that the C8A:EHO LB film is a faster sensor than the pure EHO LB film. The C8A matrix facilitates the access of the NO₂ molecules inside the film, increasing the available active sites and hence reducing the minimum concentration of NO₂ that can be optically detected. Also, the magnitude of the gas response for pure EHO films decreased quickly as the temperature was increased [10]. However, the C8A:EHO 2 LB film showed a more stable response when exposing to NO₂ and increasing the temperature. This enhanced behavior was partially attributed to the reduced porphyrin aggregation when this molecule is hosted by the C8A matrix, which would increase the available surface area of porphyrin exposed to the gas molecules and whose semi-porous structure would facilitate both the penetration (adsorption and absorption) and desorption of the toxic gas.
The capability of the C8A matrix on the EHO dis-aggregation in the mixed films has been previously demonstrated by means of UV-visible spectroscopy [13]. Due to the porphyrin aggregation, both pure EHO and C8A:EHO mixed films on water showed complex broad and red-shifted spectra with respect to the EHO solution spectrum, which is characterized by a single and narrow Soret band centred at 427 nm. However, the mixed films spectra showed a higher contribution of monomers and other less aggregated species as compared to the pure EHO film. In particular, the C8A:EHO spectrum exhibited a maximum at 438 nm and two main shoulders at 427 and 447 nm whilst the pure EHO LB film spectrum showed the maximum absorbance at 448 nm, a main shoulder at 440 nm and a small contribution at 427 nm.

In order to get deeper insight into the dis-aggregation effect of the C8A matrix and its influence on the improved response of the mixed LB films to NO\textsubscript{2} gas, the corresponding spectra were analyzed before and after the first response cycle to the toxic gas. Fig. 3 shows the spectrum of the C8A:EHO LB film (10 excursions) before any exposure (solid line) and that obtained after one cycle of exposure to NO\textsubscript{2} and the subsequent recovery with dry nitrogen (dashed line). As can be seen, the shape of both spectra is very different. The pre-exposure spectrum corresponds to that described above where some EHO aggregation remains, although not as aggregated as the pure EHO LB film. Surprisingly, the exposed and recovered spectrum exhibit a single peak centred at 427 nm, clearly corresponding to the monomeric EHO solution spectrum.

![Fig. 3. Spectra corresponding to a mixed C8A:EHO LB film (10 excursions) before any exposure to 5 ppm NO\textsubscript{2} (solid line) and after the subsequent recovery (dashed line).](image)

This interesting result gives new and definite support to the enhanced NO\textsubscript{2} sensing behavior observed for the C8A:EHO mixed LB films [13]. It is known that the porphyrin aggregation is detrimental to the gas sensing application since the interaction with the incoming gas molecules is seriously difficulted by the stacked macrocycles [3]. However, when the C8A matrix is used, the EHO molecules seem to...
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find a suitable environment that facilitates their almost complete dis-aggregation under effective interaction with the analyte molecules. It is also worth noting that the first response-recovery cycle is always slower than the following ones (data not shown), probably due to this dis-aggregation process.

After the first cycle, the non-aggregated spectral shape and the previously published fast response times [13] remains almost unaltered in all subsequent cycles. At this point, it must be mentioned that the spectra shown in Fig. 2 correspond to a pre-exposed LB film where the main contribution comes from the monomeric EHO molecules.

In summary, the use of C8A molecules as host matrix for EHO LB films not only contribute to a partial dis-aggregation of the porphyrin molecules both at the air-water and air-glass interface but also paves the way to a complete monomeric status for EHO under NO₂ gas interaction, that definitively explains the better sensing performance of the mixed LB films.

Further confirmation of the role of the calixarene matrix in the improvement of the gas sensing characteristics of the mixed LB films was obtained by AFM. Fig. 4 shows 3D AFM images of a pure EHO LB film (5 excursions) (left) and a C8A:EHO LB film (5 excursions) (right). As can be seen, the pure EHO film surface appears with bigger and smoother domains than those of the C8A:EHO LB film, which has small and sharp sites due to the presence of the calixarene. It has been shown that a relatively porous macrostructure consisting of inhomogeneous arrays of islands is advantageous for the gas sensing application, in contrast to highly uniform, ordered and densely packed classical LB film assemblies [10,11]. In this latter case, the accessibility to the internal active binding sites will be limited by a slow diffusion of the analyte gas through the dense layer, while in the former situation the porosity will promote ingress and egress of the target molecule into and from the inhomogeneous film. This is partially achieved in pure EHO LB films prepared by ultra-fast deposition (Fig. 4 (top)) that originally exhibited better gas sensing performance as compared to classical LB films containing porphyrins [10]. However, the use of the calixarene matrix clearly enhances the surface area to volume ratio (Fig. 4 (bottom)) in the mixed film, thus allowing an easier and faster penetration of the gas molecules that undoubtedly explains its even faster response [13]. Moreover, this less patchy and more perforated organization reduces the porphyrin aggregation that is known to exist inside the bigger domains of the pure EHO film, facilitating a better accessibility of the gas molecules to the active binding sites at a molecular level, which also reasserts the increased sensibility of the mixed films [13].
Another interesting parameter for the optimization of the sensor fabrication is the influence of the film thickness on the response time. The kinetics of the response and recovery processes for C8A:EHO samples ranging from 1 to 20 excursions at the Soret band wavelength (427 nm) are shown in Fig. 5. All plots can be easily divided into two phases. The first one corresponds to a fast response due to the adsorption of the NO$_2$ molecules to the most easily accessible surface sites. The second phase is much slower because of the slower diffusion effect caused by the upper layers blocking the access to the lower ones. In any case, the kinetic profile of the mixed films is much faster as compared to that of the pure EHO [10,13], with the first phase
nearly covering the totality of the absorbance change. A qualitative correlation can be clearly found between the number of excursions and the speed of the response. Samples with lower number of excursions take more time to reach the maximum absorbance change as compared to the thicker ones, where the second phase of the response is especially short.

Fig. 5. Response and recovery kinetics for 1-20 excursion C8A:EHO LB films at the Soret band wavelength (427 nm) under exposure to 5 ppm NO₂.

In order to analyze the surface morphology of the samples, AFM images of the films with different number of excursions were taken. Fig. 6 shows the AFM images obtained for the 1, 3, 5, 10 and 20 excursion C8A:EHO LB films. As can be seen, for low number of excursions the surface appears not totally covered by brighter domains. This can be related to the partial transfer of EHO molecules from the air-water interface to the glass substrate revealed in previous studies by UV-visible spectroscopy [14]. As the number of excursions increases, the surface is covered with new domains where the subsequent layers can be easily appreciated in the AFM images. Nevertheless, all 5 images show a substantial roughness of the surface, although not the same in every case. Qualitatively, the roughness of the different surfaces seems to increase with respect to the number of excursions, at least for the 1, 3, 5 and 10 excursion samples. After this, 10 and 20 excursion films appear to have a similar roughness.
Fig. 6. AFM images of a) 1, b) 3, c) 5, d) 10, and e) 20 excursion C8A:EHO films.

Some numerical parameters that can define the speed of the response may result very useful to describe the effectiveness of a gas sensor. Good parameters for this purpose are $t_{50}$ and $t_{90}$, which are, respectively, the time necessary to reach the 50% and the 90% of the total absorbance change. Also, in order to compare different surfaces regarding their roughness, a quantitative parameter for this magnitude has been used. The chosen parameter has been RMS (Root Mean Squared) roughness.

The obtained values for $t_{50}$, $t_{90}$ and the corresponding RMS roughness for C8A:EHO LB films with different number of excursions are shown in Table 1. As can be seen, for lower number of excursions the response is slow and the RMS roughness is low. As the number of excursions increases, the RMS roughness increases and the response time decreases, specially the $t_{90}$, with minimum values for 10 excursions.

**Table 1.** Average $t_{50}$, $t_{90}$ and RMS roughness.

<table>
<thead>
<tr>
<th>Number of excursions</th>
<th>Average $t_{50}$ (s)</th>
<th>Average $t_{90}$ (s)</th>
<th>RMS roughness (nm)</th>
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<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>650</td>
<td>1,325</td>
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<tr>
<td>3</td>
<td>32</td>
<td>579</td>
<td>1,875</td>
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<tr>
<td>5</td>
<td>11</td>
<td>106</td>
<td>2,432</td>
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<td>10</td>
<td>7</td>
<td>20</td>
<td>3,656</td>
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<tr>
<td>15</td>
<td>23</td>
<td>68</td>
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<td>20</td>
<td>28</td>
<td>72</td>
<td>4,020</td>
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</tbody>
</table>
This behavior is better depicted in Fig. 7, where plots of the average $t_{50}$, $t_{90}$, and RMS roughness versus the number of excursions are shown. Although the average $t_{90}$ is much higher than the average $t_{50}$, the shape of the left half of the curves (from 2 to 10 excursions) is quite similar, decreasing as the number of excursions increases. In the right half (from 10 to 20 excursions), the average $t_{50}$ increases rapidly while the average $t_{90}$ keeps almost constant. In both $t_{50}$ and $t_{90}$, the optimum number of excursions is 10, for which the response is the fastest one. Also, the slowest response is for the 1 excursion film in both parameters. The RMS roughness plot shows an increasing roughness up to the 10 excursion film. After this point, it remains almost constant when increasing the number of excursions. As can be seen, for lower number of excursions (i.e. less than 10 excursions) both $t_{50}$ and $t_{90}$ decrease as the roughness increases. For higher number of excursions this behaviour is different, increasing the speed of the response with the roughness. However, this increase in the response time is higher for the $t_{50}$ than that for the $t_{90}$.

Fig. 7. a) Average $t_{50}$ and RMS roughness versus number of excursions. b) Average $t_{90}$ and RMS roughness versus number of excursions.
A possible explanation for this phenomenon is related to the LB film homogeneity. Usually, LB films have been required to be very homogeneous, with a continuous molecular order, avoiding any kind of structural defects to have the maximum number of molecules. This leads to densely packed layers that, in fact, contain more active binding sites per layer, but in the case of gas sensing the accessibility of gas molecules to lower layers is limited by diffusion through the dense outer layers. Therefore, an irregular and porous film, with “holes” and “piles”, allows gas molecules to penetrate easier through outer layers, improving the accessibility to lower layers. The mixed C8A:EHO LB film shows these features, thanks to the presence of the C8A. As the RMS roughness increases, the film is more porous and perforated, what produces a magnification of this effect.

The different response times can be explained following the previous discussion. For low number of layers the film surface is more compact and not very rough, what makes it less accessible for the gas molecules. This can be explained in terms of available binding sites for gaseous exchange. If all the porphyrin molecules are deposited on a solid substrate, half of their binding sites will be towards the outside and the other half are going to be towards the substrate (assuming a complete flat packing of the molecules). Consequently, the sensitivity of the film will be reduced to 50% with respect to the free porphyrins. This only happens for a one-layer film where all molecules are deposited directly on the solid substrate. For films containing two or more layers, although the binding sites in the base layer remain blocked, the second and subsequent layers will not be in contact with the substrate, reducing the previous effect [11].

Also, as the number of layers increases, the surface becomes rougher and more porous, what improves the gas diffusion inside the film. When the sample reaches a high number of layers (i.e. ten or more), the last transferred layers bury pre-existing ones, keeping surface roughness almost constant while the film thickness increases. As a result of this, the number of easily accessible molecules decreases when the surface roughness stops increasing. Therefore the response speed decreases. A balanced value of layers avoids the disadvantages of compact and diffusion limiting surfaces, but without the burying effect of a high number of layers. In this work, the balanced value in which the thickness is optimum has been found to be 20 layers (10 excursions).

4. Conclusions

The mixed C8A:EHO 3:2 LB film architecture leads to a fast response NO₂ sensor, better than those made only with EHO. The presence of the C8A decreases the porphyrin aggregation and makes the surface more accessible to NO₂ molecules. After one cycle of exposure-recovery the mixed film shows no aggregation for the
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porphyrin molecule, enhancing the response for the subsequent cycles. The kinetics of the exposure to NO\textsubscript{2} has shown an important thickness dependence, what has been related to the surface roughness. By means of the AFM images analysis, it has been found that the surface roughness increases until the sample reaches 10 excursions, keeping almost constant from that point on. An optimum film thickness for fast response times has been produced by a ten excursion film for both $t_{50}$ and $t_{90}$.

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References

Selective detection of volatile organic compounds by spectral imaging of porphyrin derivatives bound to TiO$_2$ porous films

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1. Introduction

The detection of volatile organic compounds (VOCs) through electronic nose technologies has been generally based on metal–oxide semiconductors and on conducting polymer resistive materials.\textsuperscript{1,2} Such systems have shown good results for the discrimination of analytes of different chemical functionality, but the distinction of compounds from within a given chemical class continues to be a challenging task.\textsuperscript{3} Also, these materials are not appropriate for the detection of metal–binding species, when many of the most toxic and odorous compounds are excellent ligands for metal ions. Thus, detection of molecules such as amines, phosphines and thiols has been much less explored.\textsuperscript{4}

In the last few years, metalloporphyrins have been employed for the optical detection of different gases.\textsuperscript{3-9} These molecules are quite stable and their properties can be precisely tuned by modifications of their molecular structure. The sensing properties of metalloporphyrins depend on the coordinated metal, the peripheral substituents and the conformation of the macrocycle.\textsuperscript{10} Also, the organic chemistry of these compounds has been widely investigated, so that there are many synthesis routes describing the introduction of a wide range of substituents at their peripheral positions, and a high number of the metals can be coordinated to the porphyrin core.\textsuperscript{10}

The presence of $\pi-\pi$ interactions between porphyrins may cause aggregation when the molecules are deposited on solid substrates, which can result in broadening, shifting and splitting of the bands present in the spectrum with respect to the porphyrin solution.\textsuperscript{11} In the case of VOC detection, the interaction with this kind of compound may modify these interactions, resulting in modifications of the spectrum that can be used for sensing applications.\textsuperscript{10}

In the search of porphyrin–based sensors, a wide range of substrates can be used as solid support for these molecules, from glass (for example, in the Langmuir–Blodgett technique)\textsuperscript{12-14} to silica gel.\textsuperscript{3,4} Meanwhile, solar cell researchers have been sensitizing TiO$_2$ with several organic dyes for light harvesting, and some
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of them have focused their attention on porphyrins because of their efficacy in photosynthesis. As a result of this, the anchoring to TiO$_2$ has been studied for a number of functional groups, such as salicylate, sulphonic acid, phosphonic acid, acetylacetonate and one of the most widely used derivatizations, carboxylic acid.\textsuperscript{15} However, TiO$_2$ films prepared for solar cell purposes are usually thick and very dispersive, which makes them inappropriate for gas sensing when using UV–visible spectroscopy.

Recently, the preparation of columnar TiO$_2$ thin films by physical vapor deposition has been developed.\textsuperscript{16} These materials are characterized by a columnar microstructure with large and open pores which makes them very accessible to molecules originating from outside the film.\textsuperscript{17} Owing to these characteristics, these systems have been found to be ideal for the study of diffusion processes of relatively large molecules such as porphyrins.\textsuperscript{18, 19} This structure also allows fast diffusion of gaseous analytes which is necessary for the gas sensing application. On the other hand, the columnar TiO$_2$ films are thin and non dispersive, allowing optical transmission measurements. Therefore, the combination of these structural properties with the possibility of chemical anchoring of the sensing dye, makes the TiO$_2$ a very good candidate for the fabrication of porphyrin–based sensors. Another good possibility would be the use of ZnO which easily grows in nanowires and other nanostructures.\textsuperscript{20} However, the lack of stability in normal atmosphere and aqueous media is the main disadvantage of this material whose binding mechanism with the dye does not work as well as in TiO$_2$. Silica\textsuperscript{4} and ormosils\textsuperscript{21} have been also used as hosting matrices for porphyrin sensors with very nice results. However these materials are not equivalent to TiO$_2$ in any of their variants since do not allow chemical binding of the dye and therefore do not permit to exploit this particular capability. Finally, TiO$_2$ (like ZnO) also offers the possibility of using its well known photonic properties for gas sensing applications. Although the measuring set-up becomes more complicated than simple absorption spectroscopy, good sensibilities and selectivity have been found by following photoconductivity changes in the presence of several gas analytes.\textsuperscript{22}

In this work, the carboxylic acid derivatives of a free–base porphyrin and 10 of its metal derivatives (TCPPs) have been used for optical gas sensing of volatile organic compounds. For this purpose, microstructured columnar TiO$_2$ thin films have been used as hosts for the porphyrins and the chemical binding between the porphyrin and the TiO$_2$ has been confirmed through infrared spectroscopy. Also, the influence of this binding on the porphyrin aggregation and orientation has been investigated. The optical responses of the set of porphyrins to a total of 12 individual VOCs have been analyzed, and the magnitude of the spectral changes has been represented as color image patterns with spectral resolution which allows selective recognition for each analyte.
2. Experimental section

2.1 Metal oxide matrix

Transparent and amorphous TiO$_2$ films were prepared by the GAPVD (glancing angle physical vapor deposition) technique at room temperature. For UV–visible spectroscopy the films were deposited on glass substrates. For specular reflectance FT–IR spectroscopy, the films were prepared on gold coated silicon substrates. Gold coating was performed by sputtering onto silicon substrates. Evaporation was carried out by using TiO pellets in the solid state as a target, which were converted into a vapor by bombardment from a high energy electron beam. As the vapor condensed on the surface of the substrate, it forms a thin layer. This process was performed under vacuum conditions at about $10^{-4}$ torr of O$_2$ in order to obtain columnar thin films of TiO$_2$. The deposition onto the substrates was carried out using the GAPVD technique through the use of a home–made sample holder. It consisted of a 40 cm diameter steel circular plate from which the samples were hung in a vertical position. The radial separation between the evaporation center and the sample position provides the different inclinations of the substrates, relative to the direction of evaporation. Through this procedure, five angles of incidence (60º, 70º, 80º, 85º and 90º), measured between the normal to the sample and the incident direction, were obtained.

Films with a thickness in the range 150–400 nm were prepared by this method. The microstructure of these films deposited on a silicon wafer was examined by field emission scanning electron microscopy (FESEM) in a Hitachi S5200 microscope. Cross-sectional views were obtained by cleaving the silicon substrates. A common property of the obtained films is their high porosity and, as a consequence, they exhibit relatively low values of refractive index.

2.2 Porphyrins

A total of 11 porphyrins have been used in this work, one non–metalated and 10 of its metal derivatives. The structure of 5,10,15,20–tetrakis(4–carboxyphenyl)–21H,23H–porphyrin (H$_2$TCPP) is shown in Figure 1. In the metal derivatives, the two hydrogen atoms in the center of the porphyrin ring are replaced with the corresponding metal ion (i.e. Ag(II), Co(III), Cu(II), Cr(III), Fe(III), Mn(III), Pd(II), Ru(II), Sn(IV) and Zn(II)). Hereafter, compounds will be named by their metal ion followed by TCPP. All porphyrins were purchased from Frontier Scientific Europe Ltd. and were used without further purification.
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Figure 1. Molecular structure of 5,10,15,20-tetrakis(4-carboxyphenyl)-21H,23H-porphyrin. In the metal derivatives, the two hydrogen atoms in the center of the porphyrin ring are replaced with Ag(II), Co(III), Cu(II), Cr(III), Fe(III), Mn(III), Pd(II), Ru(II), Sn(IV) or Zn(II).

2.3 Binding

Binding of the dye molecules to the TiO$_2$ films was carried out by immersing the films in a 10$^{-4}$ M EtOH solution of the dye at room temperature (21 ºC) for 1 h. The infiltrated films were rinsed, immersed in EtOH to remove physisorbed dye and then dried using dry N$_2$ through a nitrogen gun. All films, which were stored in air, were dried by heating to 110 ºC for 30 min and allowed to cool to 20 ºC under a dry N$_2$ gas stream prior to the measurements.

2.4 Infrared spectroscopy

The study of the binding of the carboxylic porphyrins to TiO$_2$ was performed through specular reflectance Fourier transform infrared (FT–IR) spectroscopy using a Jasco FT/IR–6200 spectrometer. This measuring set-up provided us with enough signal for the required analysis in contrast to other arrangements with greater depth of penetration such as ATR. The specular reflectance FT–IR spectra for the porphyrins were measured neat (by casting on silicon substrates) and bound to the TiO$_2$ thin films. All spectra were obtained using typically 500 scans with a resolution of 4 cm$^{-1}$. The background was removed by subtracting the signal obtained from a gold substrate.

2.5 Gas sensing

A gas testing chamber was used to expose the samples to the VOCs. This chamber
consisted of a gas inlet and an outlet, a Peltier heating–cooling device and housings for two optical fibers that deliver and collect the light for the optical measurements. Further details regarding this setup can be found elsewhere. The fibers were connected to a World Precision Instrument Spectromate spectrophotometer. Gaseous VOCs were obtained by bubbling dry nitrogen through a bottle immersed in a temperature-controlled water bath containing the desired neat liquid analyte. By means of this procedure, the resulting gas was composed by dry nitrogen saturated in each VOC, whose concentration can be calculated through its vapor pressure at the corresponding temperature. Vapor pressures were controlled by regulating the bath temperature, 20ºC in all cases except for the VOC concentration dependence experiments where a temperature of 0 ºC was used in order to avoid a possible condensation of the analyte inside the gas chamber or the tubing system. Finally, the exact desired concentration was obtained by diluting the VOC–N\textsubscript{2} gas stream with another N\textsubscript{2} gas stream, and calculated by applying the corresponding dilution factor. Similar procedures for the generation of low ppm levels of VOC’s in nitrogen can be found in the literature.4

Prior to the gas exposure phase, dry N\textsubscript{2} was introduced through the gas inlet to allow complete desorption of possible contaminating gases from the inner walls of the chamber and thus preventing the contamination of the samples. Then, the samples were introduced into the gas chamber and again dry N\textsubscript{2} was introduced into the chamber to allow complete desorption of possible contaminating gases adsorbed on the sample. After this, the gas mixture (VOC and N\textsubscript{2}) was directed into the gas chamber until complete saturation of the porphyrin. All samples were exposed at room temperature (~293 K). For the recovery phase, dry N\textsubscript{2} was introduced again to remove all the VOC gases from the chamber. This phase occurred at elevated temperature (~383 K) to allow complete desorption of the VOCs from the samples.

2.6 Identification patterns

In order to create selective easy-to-read identification patterns, we have developed an innovative way of showing the optical response based on imaging spectroscopy. For each porphyrin and analyte, the non–exposure spectrum was subtracted from the exposure one at each wavelength and then normalized to the maximum absorbance of the non–exposed spectrum. Finally, the resulting values were squared to maximize differences. All the squared difference spectra for each analyte in the Soret band region were put together and converted into an m x n matrix (where m is the wavelength and n is the number of used porphyrins, n=11 in this case) which was represented as color image using Origin Pro 8 software. Through this representation, a barcode–like image consisting of 11 columns and m rows was created for each analyte; in which the different values (11 x m pixels) are colored from red to blue (i.e. non change points are represented in red and maximum
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change points are colored in blue).

3. Results and discussion

3.1 TiO$_2$ thin film microstructure

Cross-section and normal FESEM images corresponding to TiO$_2$ thin films prepared by GAPVD at an angle of deposition of 70º are shown in Figure 2. The cross section image shows the tilt angle of the columns and the thickness of the film. The angle formed by the columns and the substrate was found to be 60º with a film thickness of approximately 350 nm.

![Figure 2. Cross section (top) and planar (bottom) FESEM images of the columnar TiO$_2$ thin films prepared at an angle of deposition of 70º.](image)

The analysis of the images in Figure 2 reveals that the observed apertures correspond to mesopores (i.e., pores bigger than 2 nm) extending from the surface to the bottom of the film. This allows the accessibility of large molecules like porphyrins
during the composite preparation and improves subsequent applications that would require a fast diffusion of gas molecules through the film structure.

The porosity of the TiO$_2$ thin films can also be deduced from the value of their refraction index, estimated as 1.79 from the recorded and simulated UV–visible transmission spectra respectively (data not shown). This value is much smaller than that corresponding to the bulk material (i.e. 2.49 for TiO$_2$ in the form of anatase) and is a clear proof of the high porosity of the film. The low refraction index makes these films very useful for UV–visible spectroscopy applications.

All different angles of incidence (60º, 70º, 80º, 85º and 90º) showed similar properties, but in order to avoid any possible difference, all experiments were carried out using films of an angle of 70º as host material for the porphyrins. FESEM images of different films prepared with this angle were analyzed and the differences in thickness were no greater than 20 nm.

3.2 Binding to TiO$_2$

Specular reflectance FT–IR spectra of H$_2$TCPP and ZnTCPP neat and bound to TiO$_2$ are shown in Figure 3. In all cases, the existence of typical bands corresponding to the symmetric and asymmetric stretching modes of the pyrrole ring ($\nu$(C–H), $\nu$(C=C) and $\nu$(C=N)) within the meso-tetraphenylporphyrin macrocycle was evident over the range 700-1500 cm$^{-1}$. However, that which reveals the binding interaction between the TCPP and the metal oxide surface is the comparison of changes in the region of the carbonyl group in the FT–IR spectra. Neat samples of H$_2$TCPP and ZnTCPP showed a band in the region of 1685–1695 cm$^{-1}$ which is characteristic of the $\nu$(C=O) stretch and a strong band in the 1385–1415 cm$^{-1}$ region due to the $\nu$(C–O) stretch of the carboxylic acid groups. It is worth mentioning that these bands are known to shift to lower frequencies in the case of the $\nu$(C=O) stretch and to higher ones for the $\nu$(C–O) stretch due to extensive hydrogen bonding of the carboxylic acid groups in para substituted TCPPs where the –COOH groups are situated in the plane of the tetrapyrrole macrocycle.

Binding to TiO$_2$ colloidal films has been associated with the disappearance of the bands corresponding to the $\nu$(C=O) and $\nu$(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 $\nu$(CO$_2^-$) stretches respectively. These spectral changes have been found to be compatible with chelating and/or bidentate binding modes of the carboxylate groups on the TiO$_2$ surface.

In our case, the bands corresponding to the C=O and C–O stretching modes disappear only partially with a broadening of the latter, especially in the case of ZnTCPP/TiO$_2$, while the appearance of that of the symmetric $\nu$(CO$_2^-$) stretch is not so evident due to overlapping with the remaining and shifted $\nu$(C–O) stretch band. Moreover, the changes in the 1500–1750 cm$^{-1}$ region are hindered in part by the
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presence of a strong and broad band around 1630 cm$^{-1}$ corresponding to the TiO$_2$ in the columnar film. The IR spectrum of a porphyrin-free TiO$_2$ film is available in the Supporting Information (Figure S1).

The observed partial changes are therefore consistent with the presence of free carboxylic acid groups coexisting with carboxylate groups bound to TiO$_2$. In this situation, the para substituted TCPPs are likely to be bound only by one or two of its four carboxyl groups to the metal oxide surface due to its planar structure, resulting in a perpendicular orientation of the molecule with respect to the surface.$^{26,31}$ In fact, in smooth and even surfaces the flat geometry of the dye molecule would not admit another type of binding, although we can also assume that the irregular surface of the columns in the titania film allows porphyrins to bind more than two carboxylate groups and hence we could find molecules with one to four points anchored to the titania surface. In any case, most of the dye molecules are only partially anchored to the TiO$_2$ with a perpendicular orientation with respect to the surface that allows them to interact (face to face) with other molecules causing aggregation.

Figure 3. Specular reflectance FT–IR spectra of H$_2$TCPP and ZnTCPP neat (by casting on silicon substrates) and bound to TiO$_2$.

UV–visible spectra of H$_2$TCPP in EtOH solution and bound to TiO$_2$ films are shown in Figure 4. In the solution spectrum, H$_2$TCPP appears in its monomeric form with the Soret band centered at 415 nm. However, the spectrum of the porphyrin in
the film featured a broadening of the Soret band whose maximum is blue shifted (5 nm) with respect to the solution. This behavior can be mainly attributed to the formation of H–aggregates (face–to–face stacking) between porphyrin molecules, although the formation of a certain number of J–aggregates cannot be discarded.

The shifting and broadening of the absorption spectra of aggregated species in thin films, relative to the monomeric spectrum in solution, has been interpreted by the application of exciton models such as the point dipole model proposed by McRae and Kasha or the extended dipole model proposed by Kuhn and collaborators. Excellent discussions and comparisons between them can be found in the literature as well as examples of the application of these models to aggregated porphyrins when deposited as thin films. According to the point dipole approximation, and assuming that the transition moments of the chromophores are lying parallel to each other, a red shift is expected when the displacement angle between the transition moments and the line connecting their centers is smaller than 54° (J–aggregate), while a larger displacement angle will produce a blue shift (H–aggregate). In general, a Scheibe aggregate (J–aggregate) is formed when Coulomb attraction forces between the interacting dipoles outweigh repulsion. Often, this situation is predicted more accurately by the extended dipole approximation, especially at direct contact of the molecules. In the case of the porphyrins studied here, the observed blue–shift in the UV–visible spectra reveals that the dyes form H–aggregates when anchored to the TiO₂ film. However, the broadening of the Soret band indicates that along with the H–aggregates and the monomers, there are also some J–aggregates present in the film.

This result is not surprising taking into account the porphyrin binding revealed by the IR experiments where only 1 or 2 of the 4 carboxylic groups are bound to the TiO₂ matrix. With this arrangement, where the porphyrin central ring is normal to the TiO₂ surface (vertical orientation), it is expected to observe these types of π–π interactions. Depending of the exact relative position of adjacent macrocycles, determined by the anchoring site on the metal oxide surface, different types of aggregates (H or J) would be formed.

Although the porphyrin aggregation could be detrimental for its gas sensing application due to a hindered access of the analytes to the porphyrin coordination sites, it will be shown that such π–π interaction is not strong enough to avoid effective analyte binding probably due to the positive influence of the TiO₂ matrix whose chemical binding with the dye molecule prevents a closer position of their conjugated rings thus avoiding a higher degree of aggregation.
Selective detection of VOCs by spectral imaging of porphyrin/TiO$_2$ porous films

Figure 4. UV–visible absorption spectra of H$_2$TCPP in ethanol solution (solid line) and bound to a titania film (dashed line).

Although this spectroscopic characterization has been focused on the H$_2$TCPP and ZnTCPP derivatives, the rest of the metal complexes showed a similar behavior in terms of binding to TiO$_2$ and π–π interaction.

In order to assess the dye surface coverage, the porphyrin surface concentration $\Gamma$, was calculated for the different derivatives by integrating the absorption spectrum, both in solution and in the film, according to the method provided elsewhere.$^{18}$ The $\Gamma$ values were in the range 3-5 x 10$^{-9}$ mol cm$^{-2}$ depending on the porphyrin, with maximum variations below 10% of the average value in all cases.

3.3 Gas–sensitive optical properties and recognition patterns

Composite porphyrin/TiO$_2$ films obtained from each one of the 11 porphyrins have been exposed to vapors of the following 12 different analytes: acetone, acetonitrile, chloroform, butylamine, dichloromethane, diethylether, dimethylformamide, ethanol, hexanethiol, hexylamine, methanol and tetrahydrofuran. Figure 5 (top) shows the spectra of ZnTCPP and H$_2$TCPP composite films before and after their exposure to acetone. In the case of the ZnTCPP, the Soret band is red–shifted (13 nm) and increased after the exposure. The exposed H$_2$TCPP film spectrum shows less red shift (8.5 nm) and some decrease with respect to the pre–exposure spectrum. In Figure 5 (bottom), spectra of ZnTCPP and H$_2$TCPP films before and after exposure to butylamine are shown. In this case, the ZnTCPP Soret band is more red–shifted after the exposure than when exposed to acetone (17.5 nm), and the intensity of the absorbance is much more increased. However, the H$_2$TCPP spectrum shows a smaller shift (4.5 nm), and an intensity increase like in the case of the ZnTCPP derivative. In most cases, the rest of porphyrins showed significant differences of their respective spectral shifts and intensity changes when exposed to the different compounds. Through the recovery phase, samples returned to their
original status. In order to explore the repeatability and reversibility of the system, all samples were exposed and recovered several times to each of the analytes, showing no differences between cycles (data not shown).

On the other hand, the reproducibility of the response was evaluated in all cases by using the maximum variation in the absorbance change for at least 3 different films of the same porphyrin exposed to the same analyte (butylamine). The statistical analysis yielded a mean %RSD (relative standard deviation) for the response of 4.8% reaching a maximum value of 8.9% for MnTCPP. This good reproducibility is probably due to a complete saturation of the TiO$_2$ film by the infiltrated dye and the low variability in the film thickness.

The observed spectral changes demonstrate that porphyrins are a good choice for the detection of multiple analytes. In particular, the open coordination sites for axial ligation and the large spectral shifts upon ligand binding make the metalloporphyrins very appropriate for the detection of metal–ligating vapors, although other type of chemical interactions such as Lewis or Bronsted acid–base interactions, hydrogen bonding, etc. are also possible. Moreover, the different response of the different porphyrins to each analyte reveals their potential use as selective sensors by using on a proper combination of the corresponding responses.

Figure 5. Top: Before (solid line) and after (dashed line) exposure to acetone spectra of ZnTCPP/TiO$_2$ (left) and H$_2$TCPP/TiO$_2$ (right) composite films. Bottom: Before (solid line) and after (dashed line) exposure to butylamine spectra of ZnTCPP (left) and H$_2$TCPP (right) films.

A selective response can be obtained for each analyte through the analysis of the whole set of porphyrins, but owing to the large amount of collected information, a previous data processing stage is necessary in order to focus the attention on the spectral change.

A quantitative measure of the response is useful for a fast analysis which includes several porphyrins and analytes, even more in this work, where the number of
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different cases is elevated. A commonly used method comprises the subtraction of the gas exposure spectrum from the non-exposure one and the obtained difference at each wavelength is squared and then grouped in only one value by applying a summation function. The drawback of this kind of quantification is the loss of information caused by summarizing a whole spectrum (or a difference spectrum) in a numerical value. The spectral changes are characterized not only by the spectral shift in terms of wavelength values but also by the corresponding intensity of the absorbance; this is the whole spectrum profile. Such changes have been shown to be characteristic of each porphyrin and analyte, and cannot be distinguished when changes in intensity and wavelength are represented as one value alone.

In order to reduce the loss of information, an innovative way of showing the response of all porphyrins to a certain analyte is shown in Figure 6. The resulting images possess spectral resolution and can be interpreted as recognition patterns for each analyte. Through these patterns, the shift and the change in absorbance intensity can be easily distinguished. By means of these images, like in the case of using bar codes, both the position and the intensity of the different bands give information about the compound to be identified. Each pattern consists of 11 columns corresponding to the 11 porphyrins used in this work. Every column shows the squared average difference of the post- and pre-exposure spectra in a color scale from red to blue, where red corresponds to no change between exposed and non-exposed spectra and blue is the highest change detected. As detailed in the experimental section, this method maintains all the information regarding the intensity changes at each wavelength of the Soret band region. Another interesting method found in the literature consists of a color RGB difference image of a spot of the porphyrin samples before and after exposure to the target analyte. In that case, only 3 values related to the difference spectrum (red, green and blue of an 8-bit color palette) are used for the identification pattern. Although this method has shown excellent sensing capabilities in terms of selectivity and analyte discrimination, a possible loss of information regarding the spectral changes cannot be discarded since such spectral changes contain a potential identification value at each wavelength of the spectrum. Therefore, an image containing all these changes can be nowadays an ideal identification pattern given that cheap and versatile image-reading devices are available in the market. Additionally, the proposed approach is ready to access other spectral regimes such as the infrared, provided that new materials with sensing activity in that range are used, which enables this identification system to exploit optical sensing beyond the human-vision-based RGB colorimetric systems.

As can be seen in Figure 6, each analyte has a characteristic pattern that differs from the rest in one way or another, allowing the virtual identification of all analytes. Although some compounds show similarities to others, for example, acetone and acetonitrile or chloroform and dichloromethane have similar patterns, they are not
identical.

In particular, butylamine, hexylamine, hexanethiol and dimethylformamide are the analytes that produce the highest values of change, especially when the exposed porphyrin is ZnTCPP. On the other hand, the exposure to acetone or diethylether results in a low response. In order to further improve our discrimination capability, new strategies comprising the use of new porphyrin derivatives with more efficient structures are under study. Regarding the porphyrin behavior, ZnTCPP is by far the most responsive. Other derivatives, such as CrTCPP or FeTCPP, show low values of response. However, this cannot be considered a drawback since it is known that a highly selective odor sensing device (like the human olfactory system) must consist of a combination of highly responsive receptors with reduced selectivity and highly selective ones that usually show low response values. At this point, it is worth to mention that multiple gas sensing should be demonstrated before a wider range of real applications can be proposed. Nonetheless, single gas detection is possible with the proposed system and it capability for the analysis of mixtures in now under investigation.

A future integration of the sensing films into a sensor array would imply the use of a parallel multiple fiber-optic set-up and a mechanical arrangement to measure sequential layers, in such a way that the resulting identification images would be obtained in real time.

**Figure 6.** Identification patterns obtained for the different analytes. Color scale goes from red to blue, where red means no change between exposed and non–exposed spectra and blue is the highest change detected.
3.4 Concentration dependence and kinetics of the gas exposure and recovery

The development of a sensor involves the search of some specific characteristics. A good sensor must be selective, and its response needs to be fast, reproducible, reversible and concentration–dependent for quantification purposes.

The kinetics of the TCPPs/TiO$_2$ films response when exposed to the different VOCs was analyzed by following the time evolution of the absorbance at the wavelength of its maximum change. The ZnTCPP/TiO$_2$ film response to EtOH is provided as an example in Figure 7. This figure depicts a sequence of five consecutive EtOH gas exposure–recovery cycles of a ZnTCPP composite film in which the EtOH concentration has been increased after each recovery phase. These cycles were obtained by bubbling dry N$_2$ through liquid EtOH at a temperature of 0 ºC and diluting the resulting gas stream with another N$_2$ stream in the appropriate proportion. As can be seen, increasing concentrations of EtOH result in an increase in the magnitude of response, indicating that the sensor behavior is concentration–dependent. Therefore, the system is also suitable to be used for quantification purposes. A wider concentration range was tested with identical results down to ~100 ppm EtOH (see Figure S2).

An evaluation of the concentration dependence of the response can be obtained by applying an isotherm model, which describes the adsorption/desorption equilibrium of the gas molecules onto the solid surface. The Langmuir adsorption isotherm$^{48}$ has been used to characterize the adsorption of many types of molecules onto different materials.$^{49-51}$ It is usually expressed by:

$$\frac{n_{ads}}{N_s} = \frac{\lambda c}{1 + \lambda c}$$  \hspace{1cm} (1)

where $n_{ads}$ is the number of gas molecules adsorbed (which is proportional to the change in Soret band absorbance, $\Delta$Absorbance), $N_s$ is the number of adsorption sites, $\lambda$ is a constant relating to the adsorbability of the gas and $c$ is the concentration of the gas, [EtOH]. Rearrangement of eq. (1) leads to the linear form of the Langmuir adsorption isotherm:

$$\left(\frac{c}{n_{ads}}\right) = \left(\frac{c}{N_s}\right) + \left(\frac{1}{N_s \lambda}\right)$$  \hspace{1cm} (2)

Therefore a plot of $c/n_{ads}$ versus $c$ should yield a straight line if the data points follow the Langmuir model. Fig. 7 (inset) shows a plot of $c/\Delta$Absorbance vs. $c$, and a straight line is obtained, indicating that Langmuir adsorption, even with its limited assumptions, provides a basic understanding of the EtOH–ZnTCPP interaction during the sensing process. According to the assumptions of the Langmuir model, it can be concluded that the activation energy of adsorption is the same for all binding sites in the thin film assembly, that there are a fixed number of localized surface sites present on the surface and that EtOH molecules striking a surface site that is already
occupied do not adsorb.

The Langmuir adsorption model was applied to the exposure of all TCPPs/TiO$_2$ films to butylamine gas and to the exposure of ZnTCPP/TiO$_2$ films to all 12 used analytes (see Tables S1 and S2 in the Supporting Information). In all cases a straight line was obtained, indicating that our system follows the Langmuir model.

In order to know quantitatively the speed of response, the value of $t_{50}$, which is the time taken for the absorbance to reach the 50% of its total maximum change, was calculated. In the case of the ZnTCPP/TiO$_2$ film response to EtOH, the obtained value was approximately 4.5 seconds in all cycles, revealing a very fast response process. As for the Langmuir model, $t_{50}$ was calculated for the exposure of all TCPPs/TiO$_2$ films to butylamine gas and to the exposure of ZnTCPP/TiO$_2$ films to all 12 used analytes (Tables S1 and S2, Supporting Information). In all cases, the response was found to be very fast ($t_{50} \sim 4–9$ seconds). Such behavior can be attributed to two probable reasons. On the one hand, the speed of the response is related directly to the sensitivity of the used porphyrins. On the other hand, the properties of the titania film play an important role. The microstructured film is highly porous, which leads to an easy diffusion of the gas molecules through the surface and therefore every porphyrin is exposed to the analyte without any delay.

Overall, the set of porphyrins have shown good capabilities for gas sensing with interesting odor detection applications. The response has been found to be very selective, allowing the identification of the different analytes. Also, the composite porphyrin/TiO$_2$ films have yielded fast and concentration-dependent responses, making the quantification of the volatile compounds possible through calibration curves based on the Langmuir isotherm.

![Figure 7. Kinetics of the exposure of a ZnTCPP composite film to EtOH gas at a wavelength of 430 nm. Inset: Langmuir adsorption plot for a ZnTCPP composite film.](image-url)
4. Conclusions

Microstructured columnar TiO$_2$ thin films prepared by GAPVD have been used as host materials of several porphyrins. These films are non–dispersive and hence appropriate for UV–visible spectroscopy. Also, its porous microstructure allows gas diffusion through the film, making them suitable for gas sensing.

Several porphyrins, featuring carboxylic groups that allow chemical binding to titania, have been bound to the columnar TiO$_2$ thin films and exposed to a wide range of volatile compounds. When hosted in the film, the porphyrins featured a blue shift and broadening of the Soret band, which has been attributed to the formation of H–aggregates (face–to–face stacking) between porphyrin molecules.

The gas–sensitive properties of the composite films have been studied, showing a good selectivity to the analyzed volatile compounds. For each analyte, an image–like identification pattern based on spectral imaging has been obtained, which facilitates the straightforward recognition of every compound. The responses were found to be concentration dependent, allowing analyte quantification through calibration curves. The kinetics of the exposure to several analytes showed a fast response, with a value of $t_{50}$ of a few seconds, which arises from both the sensitivity of the porphyrins and the high porosity of the TiO$_2$ films. Although the system has not yet been tested with mixed gases, it has been proven to be valid for the identification and quantification of individual VOCs.

Acknowledgments

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References

Selective detection of VOCs by spectral imaging of porphyrin/TiO$_2$ porous films

2003, 107, 8981-8987.


Supporting Information

Figure S1. Specular reflectance FT–IR spectrum of a TiO₂ film.

Figure S2. Kinetics of the exposure of a ZnTCPP composite film to EtOH gas in the range of 105 – 10500 ppm at a wavelength of 430 nm. Inset: Langmuir adsorption plot for a ZnTCPP composite film.
Selective detection of VOCs by spectral imaging of porphyrin/TiO$_2$ porous films

**Table S1.** Langmuir adsorption model results and $t_{50}$ obtained for a ZnTCPP/TiO$_2$ composite film exposed to 12 different analytes

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Analyte</th>
<th>Intercept</th>
<th>Slope</th>
<th>$R^2$</th>
<th>$t_{50}$ (s)</th>
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<td>ZnTCPP</td>
<td>Acetone</td>
<td>95.16452</td>
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<td>ZnTCPP</td>
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<td>ZnTCPP</td>
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<td>0.99134</td>
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<td>ZnTCPP</td>
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<td>ZnTCPP</td>
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**Table S2.** Langmuir adsorption model results $t_{50}$ obtained for 11 different TCPP/TiO$_2$ composite films exposed to butylamine

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<th>Porphyrin</th>
<th>Analyte</th>
<th>Intercept</th>
<th>Slope</th>
<th>$R^2$</th>
<th>$t_{50}$ (s)</th>
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<td>ZnTCPP</td>
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Anchoring effect on (tetra)carboxyphenyl porphyrin/tio_2 composite films for VOC optical detection

1. Introduction

Detection of volatile organic compound (VOC) has been generally performed through the separation and identification of components using gas chromatography or similar techniques. These analyses, although accurate, are usually time-consuming and need a lot of post-processing. Alternatively, electronic nose technologies have been used to detect several kinds of compounds by an array of different sensors, providing an instantaneous and holistic response to the particular gas. These devices are generally based on metal-oxide semiconductors and on conducting polymers. They are appropriate for the discrimination of analytes of different chemical functionality, but not when these are within the same chemical class, or when we try to detect metal-binding species.

Porphyrins and other dyes have been widely used in the last decades for gas-sensitive purposes. Their photochemical and photophysical properties make them ideal candidates for the optical detection of analytes. Thus, they can be precisely tuned by introducing substituents in their structure or coordinating metals to the porphyrin core. However, one of the most challenging points of the development of a sensor based on porphyrins is the deposition onto solid substrates. Techniques such as Langmuir-Blodgett (LB), spin-coating or casting can be used to obtain solid films of the dyes, but the organization of these films in terms of molecular aggregation is sometimes unsatisfying, mainly because of the strong π–π interaction between porphyrins, which can strongly prevent a proper response to the analytes. Several methods have been studied in order to avoid aggregation. In LB films, the addition of host molecules such as calixarenes has been found to reduce aggregates and hence improve the sensing properties of the films. Spin coating and casting techniques may involve the use of polymers or other kind of molecules when the interaction between the substrate and the deposited material is weak, creating a host structure that improves the properties of the film and in some cases partially avoids porphyrin aggregation. Although the films made with these techniques can be improved using host molecules, there are other drawbacks. Despite the fact that LB films can be made under a high control of the quantity and
Anchoring effect on porphyrin/TiO$_2$ composite films for VOC optical detection

Orientation of molecules, the technique is time consuming and the controlled structure does not always result in a substantial improvement of the sensing capabilities of the film. On the other hand, spin coating and casting are straightforward techniques useful for the fast fabrication of porphyrin films, but the control over the structure and the amount of sensing material in the film may be minimal, especially in the case of casting.

Originally developed by solar cell researchers, the use of carboxylic acid derivatized molecules and their ability to chemically bind to TiO$_2$ allows the easy fabrication of stable composite films. However, TiO$_2$ films prepared for solar cell purposes are usually thick and very dispersive, and thus inappropriate for gas sensing when using UV–visible spectroscopy. Microstructured TiO$_2$ films prepared by glancing angle physical vapor deposition (GAPVD) provide the perfect substrate for these composite films, given their transparency, high porosity, low refractive index and controlled thickness. Films prepared by this technique have been used previously for gas sensing purposes and have been found to enhance the sensing properties of the porphyrins due to their open pores that facilitates the access to incoming gaseous molecules. Also, the conformation of the sensing molecule in these composites can be important, determining its chemical binding to the substrate, according to the spatial distribution of anchoring points, and may also influence its tendency to aggregate with other molecules. A change in the position of the peripheral substituents in a porphyrin can lead to different aggregation status that may improve its sensing capabilities.

In a previous work, we reported the gas-sensitive properties of 5,10,15,20-tetrakis(4-carboxyphenyl)-21H,23H-porphyrin and 10 of its metal derivatives, using microstructured columnar TiO$_2$ thin films prepared by GAPVD as host materials. The study of the chemical binding between these para-substituted tetracarboxyphenyl porphyrins and titania revealed that the dye molecules were likely to be bound by only one or two of their four available carboxylic acid groups, leading to a specific anchoring with the porphyrin rings lying perpendicular with respect to the TiO$_2$ surface which allowed face to face interaction. The gas sensing capabilities of the composite porphyrin/TiO$_2$ thin films showed fast, selective and concentration-dependent responses to the analyzed VOCs. However, it is known that the lack of aggregation enhances the sensing properties of porphyrins, allowing the gas molecules a better access to their coordination sites. Therefore, the sensing system based on composite porphyrin/TiO$_2$ thin films may be improved by avoiding dye aggregation.

On the other hand, para and meta substituted tetraphenyl porphyrins are known to exhibit a different molecular structure. While the substituents in the para position of the phenyl groups are situated in the plane of the molecule, the meta substituents are placed in a perpendicular direction with respect to the porphyrin
ring. Based on this different molecular architecture, it has been demonstrated that para tetracarboxyphenyl porphyrins only anchor to the TiO$_2$ by one or two of the four carboxylic groups lying perpendicular to the metal oxide surface, while the meta derivatives can bind its four COOH groups lying parallel to the TiO$_2$ surface. Our hypothesis is that these different arrangements can lead to a different aggregation status of the porphyrin that may influence its sensing capabilities, either in terms of response magnitude or kinetics.

In this work, we studied composite films made of microstructured columnar TiO$_2$ and, respectively, Zn-(II)-5,10,15,20-tetra(4-carboxyphenyl)porphyrin ($m$-ZnTCPP, Figure 1a) and Zn-(II)-5,10,15,20-tetra(3-carboxyphenyl)porphyrin ($p$-ZnTCPP, Figure 1b), and their sensing properties regarding both the anchoring to the TiO$_2$ and the molecule aggregation are compared. For this purpose, the chemical binding between the porphyrin and the TiO$_2$ has been confirmed through infrared spectroscopy. Besides, the influence of this binding on the aggregation and orientation of porphyrin molecules has been investigated. The optical responses of the two porphyrins to a total of 6 individual VOCs have been analyzed to test if the different peripheral substituent position plays an important role on the gas-sensing properties of these molecules.

2. Material and methods

2.1 Porphyrins and reagents

All porphyrins were purchased from Frontier Scientific, Inc. and used without further purification. All reagents were purchased from Sigma-Aldrich and used as received without further purification.
2.2 Film preparation

We prepared transparent and amorphous TiO$_2$ columnar films by the GAPVD technique at an angle of deposition of 70° with respect to the evaporation source. The angle formed by the columns and the substrate was approximately 60°, with a film thickness of approximately 350 nm exhibiting an elevated porosity (total pore volume of 49 %) with void apertures on the surface in the form of mesopores (pore diameter > 2 nm), that also determines a relatively low refractive index value, that was found to be 1.79. Further details regarding film preparation, SEM images and structural information can be found elsewhere. The high porosity of the films would allow the accessibility of both porphyrins during the composite film preparation and VOCs during the gas sensing experiments. For specular reflectance Fourier transform infrared (FT–IR) spectroscopy, the films were deposited on gold-coated silicon substrates. Films for UV-visible spectroscopy were prepared on glass substrates. Binding of porphyrins to the TiO$_2$ films was performed by immersion of the substrates in a 10$^{-4}$ M MeOH solution of the dye for 1 h. After this, the films were rinsed with MeOH to remove physisorbed dye molecules and dried in air. Prior to the measurements, all films were heated to 110 °C for 30 min to desorb any contaminant and allowed to cool to room temperature (21 °C) under a dry N$_2$ stream.

2.3 Infrared and UV-visible spectroscopy

We performed the study of the binding of the carboxylic porphyrins to TiO$_2$ through specular reflectance FT–IR spectroscopy using a Jasco FT/IR–6200 spectrometer. The specular reflectance FT–IR spectra for the porphyrins were measured neat (by casting on silicon substrates) and bound to the TiO$_2$ thin films. All spectra were obtained using typically 500 scans with a resolution of 4 cm$^{-1}$. To remove the background, we subtracted the signal obtained from a gold substrate. UV-visible spectra of the porphyrins were recorded in MeOH solution using an Ocean Optics USB4000 spectrophotometer.

2.4 Gas exposure

We used a gas testing chamber connected through optical fibers to a World Precision Instruments SpectroMate spectrophotometer to expose the samples to the VOCs and register their UV-vis spectrum simultaneously. The chamber consisted of a gas inlet and an outlet, a Peltier heating–cooling device and housings for the two optical fibers that deliver and collect the light for the optical measurements. Further details regarding this setup can be found elsewhere. We obtained the gaseous VOCs by bubbling dry nitrogen through a bottle containing the desired liquid VOC immersed in a temperature-controlled water bath. The resulting gas was composed
by dry nitrogen saturated in each VOC, whose concentration can be calculated through its vapor pressure at the corresponding temperature. Vapor pressures were controlled by regulating the bath temperature, 20 °C in all cases except for the VOC concentration dependence experiments where a temperature of 0 °C was used in order to avoid a possible condensation of the analyte inside the gas chamber or the tubing system. In order to obtain the exact desired concentration, we diluted the VOC–N\textsubscript{2} gas stream with another N\textsubscript{2} gas stream, and calculated the final concentration by applying the dilution factor. Analogous procedures for the generation of low concentrations of VOCs can be found in the literature.\textsuperscript{6}

Immediately before the gas exposure phase, we introduced dry N\textsubscript{2} in the gas chamber to desorb completely any possible contaminating gases from the inner walls and hence preventing the contamination of the samples. Then, we inserted the samples into the gas chamber and again dry N\textsubscript{2} was introduced into the chamber to allow complete desorption of possible contaminating gases adsorbed on the sample. After this, we directed the gas mixture (VOC and N\textsubscript{2}) into the gas chamber until complete saturation of the porphyrin, typically a few seconds as detailed elsewhere.\textsuperscript{17}

We exposed all samples to the gases at room temperature (~293 K). For the recovery phase, we introduced dry N\textsubscript{2} again while heating the samples at relatively high temperature (~383 K) to remove all the VOC gases from the chamber and the samples.

2.5 Data analysis

The study of differences between before and after exposure spectra was accomplished by the analysis of the absolute value of the difference spectrum, obtained in each case by subtracting the non-exposure spectrum to the exposure one and calculating the absolute values of the absorbance corresponding to each wavelength.

In order to compare easily the different responses of the porphyrins to the analytes, we created identification patterns for each case, resulting in an image which shows the behavior of each of the porphyrins to the VOCs vapors. For each porphyrin and analyte, we subtracted the non-exposure spectrum from the exposure one at each wavelength and normalized to the maximum absorbance of the non-exposed spectrum. All the difference spectra in absolute value for each porphyrin in the Soret band region were converted into an m × n matrix (where m is the wavelength and n is the number of analytes, n = 6 in this case) which was represented as color image using Origin Pro 8 software. Through this representation, a barcodelike image consisting of 6 columns and m rows, in which the different values (m × 6 pixels) are colored from red to blue (i.e., non change points are represented in red and maximum change points are colored in blue), was created for each porphyrin.
3. Results and discussion

3.1 Binding to TiO$_2$

Specular reflectance FT–IR spectra of meta and para porphyrins neat and bound to TiO$_2$ are shown in Figure 2. In all cases, the existence of typical bands corresponding to the symmetric and asymmetric stretching modes of the pyrrole ring ($\nu$ (C–H), $\nu$ (C=C) and $\nu$ (C=N)) within the meso-tetraphenylporphyrin macrocycle was evident over the range 700-1500 cm$^{-1}$. The binding interaction between the TCPP and the metal oxide surface is revealed by the comparison of changes in the region of the carbonyl group in the FT–IR spectra. Neat samples of $m$-ZnTCPP showed two strong bands at 1732 cm$^{-1}$ and 1294 cm$^{-1}$ which are characteristic of the $\nu$ (C=O) stretch and the $\nu$ (C–O) stretch of the carboxylic acid groups, respectively. In the case of $p$-ZnTCPP, where the –COOH groups are situated in the plane of the tetrapyrrole macrocycle, the extensive hydrogen bonding of the carboxylic acid groups resulted in a shift to lower frequency of the $\nu$ (C=O) stretch at 1690 cm$^{-1}$ and an shift to higher frequency of the $\nu$ (C–O) stretch at 1402 cm$^{-1}$.22

![Figure 2](image-url)  
**Figure 2.** Specular reflectance FT–IR spectra of $m$-ZnTCPP and $p$-ZnTCPP neat (by casting on silicon substrates) and bound to TiO$_2$.

Upon binding of $m$-ZnTCPP to TiO$_2$, the $\nu$ (C=O) and $\nu$ (C–O) stretching modes disappeared completely, and new bands appeared in the 1385–1440 cm$^{-1}$ and
1530–1570 cm\(^{-1}\) regions, corresponding to the symmetric and asymmetric \(\nu\) (CO\(_2\)) stretches, respectively. In the case of \(p\)-ZnTCPP/TiO\(_2\), the bands corresponding to the C=O and C–O stretching modes were still partially present with a slight broadening of the latter. In this case, the appearance of the band corresponding to the symmetric \(\nu\) (CO\(_2\)) stretch is not so evident due to overlapping with the remaining \(\nu\) (C–O) stretch band. Moreover, the changes in the 1500–1750 cm\(^{-1}\) region, where the asymmetric \(\nu\) (CO\(_2\)) stretch band was expected to appear, were hindered by the presence of a strong and broad band around 1630 cm\(^{-1}\) corresponding to the free TiO\(_2\) molecules of the columnar film (Figure S1 in the Supporting Information).

Chemical binding of carboxylic acids to TiO\(_2\) colloidal films has been associated with the disappearance of the bands corresponding to the \(\nu\) (C=O) and \(\nu\) (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 \(\nu\) (CO\(_2\)) stretches respectively.\(^{18}\) These spectral changes have been found to be compatible with chelating and/or bidentate binding modes of the carboxylate groups on the TiO\(_2\) surface.\(^{18,23–26}\)

The IR spectrum of \(m\)-ZnTCPP/TiO\(_2\) was consistent with the absence of free carboxylic acid groups, given that C=O and C–O stretching modes disappeared completely. This suggests a planar situation of the porphyrin macrocycle with respect to the titania surface in which all carboxyl groups are bound to the TiO\(_2\).\(^{18}\) However, in the case of \(p\)-ZnTCPP/TiO\(_2\), the stretching modes corresponding to C=O and C–O disappeared only partially, indicating the presence of free carboxylic acid groups coexisting with carboxylate groups bound to TiO\(_2\). As a result of this, and due to the planar structure of the \(para\) substituted porphyrins, it can be expected that they are bound only by one or two of its four carboxyl groups to the metal oxide surface, resulting in a perpendicular orientation of the molecule with respect to the surface that allows them to interact (face to face) with other molecules, causing aggregation.\(^{18,27}\)

### 3.2 Aggregation of dye molecules

In the UV–visible solution spectra, both \(m\)-ZnTCPP and \(p\)-ZnTCPP appeared in their monomeric form with the Soret band centered at 423 nm (Figure 3). When bound to the TiO\(_2\), \(m\)-ZnTCPP showed a slight broadening of the Soret band (Figure 3a), although its peak remained at 423 nm as the solution spectrum, indicating that the porphyrin was predominantly in its monomeric form. However, the spectrum of \(p\)-ZnTCPP in the film featured a broadening and blue shift (10 nm) of the Soret band with respect to the solution spectrum (Figure 3b), which indicated that the dye molecules were arranged mostly as H–aggregates.\(^{18,28,29}\) The broadening of the Soret band has been attributed to the coexistence of monomers alongside of H and J aggregates, where the main peak is centered at the wavelength of the predominant
Anchoring effect on porphyrin/TiO$_2$ composite films for VOC optical detection

Figure 3. UV–visible absorption spectra of (a) $m$-ZnTCPP and (b) $p$-ZnTCPP in methanol solution (solid line) and bound to TiO$_2$ film (dashed line).

The results from the IR experiments support these assumptions. In the case of $m$-ZnTCPP, where all carboxylic groups are bound to the titania substrate, the macrocycle lies parallel to the surface avoiding contact between porphyrin rings and hence preventing aggregation. This is not the case of $p$-ZnTCPP, which is presumably bound to the TiO$_2$ matrix by only two of its four carboxylic groups, leaving the porphyrin ring normal to the surface and allowing π–π interactions between nearby molecules. With this arrangement, the formation of H or J aggregates is determined by the relative position of adjacent porphyrin molecules, according to the microstructure of the substrate where they are anchored.

Porphyrrin aggregation may hamper the access of the gaseous analytes to the porphyrin coordination sites, and hence be unfavorable for gas sensing purposes. Although the interaction between macrocycles might not be strong enough to impede analyte binding, the lack of aggregation is beneficial for gas sensing purposes because it allows porphyrin π systems to be completely available to incoming gaseous molecules.

3.3 Gas sensing

Composite porphyrin/TiO$_2$ films prepared with $m$-ZnTCPP and $p$-ZnTCPP were
exposed to acetone, acetonitrile, butylamine, chloroform, ethanol and tetrahydrofuran. To study the differences in their sensing performance, the difference spectra of the composite films upon their exposure to acetone, acetonitrile and tetrahydrofuran, in absolute value, alongside with the non-exposed and exposed spectra, have been analyzed (Figure 4). All samples featured important changes in their spectra during the exposure to the analytes, confirming the ability of porphyrins for the detection of VOCs. Specifically, metalloporphyrins are known for their ability to detect metal-ligating compounds because of their notable spectral changes upon ligand interaction and their open coordination sites for axial ligation.\textsuperscript{7,31}

![Figure 4. Top: Pre-exposure (solid line), exposure (dashed line) and difference (dashed dotted line) spectra of \textit{m}-ZnTCPP/TiO\textsubscript{2} (left) and \textit{p}-ZnTCPP/TiO\textsubscript{2} (right) composite films upon exposure to acetone, acetonitrile and tetrahydrofuran.](image-url)

Focusing on the difference spectra, which allow a better comparison of the spectral changes among the cases studied here, \textit{m}-ZnTCPP response was different when exposed to the three VOCs, whereas \textit{p}-ZnTCPP spectral changes were more uniform in the three cases. It can be seen that the relative heights of the two peaks in the \textit{m}-ZnTCPP difference spectra are different in each case, suggesting a more selective response to the analytes. In the acetone difference spectrum, the left peak is clearly higher than the right one, while in contrast, the behavior of the exposure to tetrahydrofuran is the opposite and the exposure to acetonitrile resulted in a
difference spectrum with two peaks of approximately the same height. On the other hand, the changes exhibited by \( p \)-ZnTCPP after the exposure to the VOCs were very similar, being the relative heights and shapes of the peaks corresponding to the difference spectra almost identical. With this information, we can expect a better sensing performance from the \textit{meta} substituted porphyrin in terms of selectivity.

Metal derivatives of \( p \)-TCPP have shown to be good candidates for the construction of selective optical sensors.\textsuperscript{17} In this case, a large number of metal derivatives is needed to ensure a good selectivity through the use of recognition patterns. Such selectivity can be significantly improved by the use of \( m \)-TCPPs since their absorbance spectrum is not affected by aggregation, with a narrower Soret band in its monomeric form being able to exhibit more specific changes in the presence of the different analytes. Moreover, this lack of aggregation can also improve the sensor sensibility through more pronounced spectral changes and its speed of response.

The spectral changes observed during the exposure of the composite films to all analytes are available in the Supporting Information (Figure S2). Upon exposure to the different compounds, all samples experienced significant changes in their respective spectra. All films returned to their initial status after the recovery procedure. Repeatability and reversibility of the system was confirmed through the cyclic exposure and recovery of the samples to the analytes, finding no differences between cycles.

In order to quantify the spectral response of the two porphyrins to all VOCs, we defined the change fraction as the area of the difference spectrum, obtained by subtracting the exposed spectrum to the unexposed one, divided by the area of the unexposed spectrum. The value that is obtained through this procedure gives an idea of the quantity of change that a porphyrin experiences, referred to its initial spectrum to make all responses comparable irrespective of the quantity of material deposited in the film. The change fraction for each case is shown in Figure 5. In all cases, \( m \)-ZnTCPP showed a higher response than \( p \)-ZnTCPP, being the difference of at least 10\%. This was especially relevant in the detection of butylamine, ethanol and tetrahydrofuran, where the \textit{meta} substituted porphyrin yielded a response between 50 and 95\% higher than \( p \)-ZnTCPP, according to their change fraction. Similar representations that summarize the spectral changes of porphyrins for gas-sensing purposes can be found in the literature.\textsuperscript{32} As was observed in Figure 4, both porphyrins showed good sensing capabilities to the selected compounds. This is confirmed by the change fraction values, which ranged from 0.2 to 1, showing that in all cases the spectra changed appreciably. However, it is noticeable that \( m \)-ZnTCPP featured a higher response to the analytes than \( p \)-ZnTCPP, indicating that aggregation between porphyrin molecules may be detrimental for gas sensing purposes.
The quantification of the spectral change provided us an easy way of comparing the gas sensing properties of the two analyzed porphyrins, but in this process some of the information contained in the spectra, such as the shape of the peaks or the wavelengths where they are located is necessarily discarded. By the creation of identification patterns we incorporated all the information provided by the spectra into a single image that depicts graphically the behavior of the sensing system (Figure 6). A similar procedure has been used previously to create fingerprints for several VOCs based on the changes that they induced to the sensing material. At a glance, it can be noticed that the patterns in $m$-ZnTCPP showed more variations among analytes than in the case of $p$-ZnTCPP. A more in-depth analysis of the images reveals that all bands corresponding to the different analytes in $m$-ZnTCPP showed appreciable differences among them, either in intensity or in position, which can be translated into a better selectivity of the system. On the contrary, $p$-ZnTCPP identification patterns were clearly more uniform. In particular, the patterns corresponding to acetone, acetonitrile and tetrahydrofuran are almost identical. In this case, the discrimination of these analytes using only the spectral information provided by the para substituted porphyrin would be difficult.
3.4. Sensor kinetics

To assess the influence of the peripheral substituents on the porphyrin performance, the kinetics of \( m \)-ZnTCPP/TiO\(_2\) and \( p \)-ZnTCPP/TiO\(_2\) films was studied. For this purpose, the composite films were exposed to 100 ppm EtOH and their absorbance at the wavelength of maximum change was recorded through time (Figure 7). The exposure of the porphyrins to EtOH resulted in an increment of the absorbance at the measured wavelength (433 nm for \( m \)-ZnTCPP and 431 nm for \( p \)-ZnTCPP) as a result of the interaction with the analyte. The spectra of both porphyrins returned to their original status during the recovery phase. To provide a quantification for the different kinetics in each case, the value of \( t_{50} \), which is the time taken for the absorbance to reach the 50% of its total maximum change, was calculated. Mean \( t_{50} \) after three cycles of exposure-recovery was 1.56 s in case of \( m \)-ZnTCPP, and 3.2 s for \( p \)-ZnTCPP. The fast responses can be attributed to the high responsiveness of Zn porphyrins\(^{17}\) and to the TiO\(_2\) porous matrix, which allows a fast diffusion of gases through its internal structure, making them instantly available to the dye molecules.\(^{14}\) However, regarding the comparison of our two systems, \( m \)-ZnTCPP kinetics was twice as fast as \( p \)-ZnTCPP. The differences in the speed of response, altogether with the results from the change fraction comparison and the identification patterns analysis, show that \( m \)-ZnTCPP/TiO\(_2\) films exhibited better gas-sensing properties than those based on \( p \)-ZnTCPP. This confirms that the positioning of the carboxylic acids in \emph{meta} position in the porphyrins studied here improves considerably the sensing capabilities of the porphyrin/TiO\(_2\) system. Therefore, our hypothesis that a change in the position of the peripheral substituents
in a porphyrin can lead to different aggregation status that may improve its sensing capabilities, either in terms of response magnitude or kinetics can be validated.

![Figure 7. Kinetics of the exposure of \textit{m}-ZnTCPP (433 nm) and \textit{p}-ZnTCPP (431 nm) composite films to 100 ppm EtOH vapor.](image)

**Figure 7.** Kinetics of the exposure of \textit{m}-ZnTCPP (433 nm) and \textit{p}-ZnTCPP (431 nm) composite films to 100 ppm EtOH vapor.

### 4. Conclusions

Composite porphyrin/TiO$_2$ films based on microstructured columnar TiO$_2$ as host material and either \textit{para} or \textit{meta}-substituted Zn tetracarboxyphenyl porphyrins as sensing molecules have been prepared. Specular reflectance FT–IR has confirmed that the chemical binding of the two porphyrins to the TiO$_2$ is different depending on the corresponding position of the carboxylic acid groups. In particular, the dye molecules with the COOH groups in \textit{meta} position were bound by their four carboxylic groups, whereas two or three of these groups remained unanchored in the \textit{para} derivative. When hosted in the film, \textit{p}-ZnTCPP featured a broadening and blue shift of the Soret band with respect to the solution spectrum, which indicated that the dye molecules were arranged mostly as H–aggregates. In contrast, the spectrum of \textit{m}-ZnTCPP remained in its monomeric form, which has been attributed to the planar anchoring by the four carboxylic groups to the titania matrix that would prevent porphyrin aggregation.

The gas-sensitive properties of the \textit{m}-ZnTCPP and \textit{p}-ZnTCPP/TiO$_2$ composites have been studied by analyzing the spectral changes undergone by the porphyrins in the UV-visible region upon their exposure to six different VOCs. All samples featured important changes in their spectra during the exposure to the analytes, confirming the abilities of these systems for the detection of VOCs. However, the response magnitude, quantified through the creation of the change fraction parameter, was considerably higher for \textit{m}-ZnTCPP as compared to \textit{p}-ZnTCPP. Furthermore, the use of identification patterns based on spectral images clearly shows that the \textit{meta}
derivative offers a more selective response to the different analytes, paving the way for the preparation of multisensor arrays based on metal derivatives of $m$-TCPP with enhanced selectivity towards isolated and mixed analytes. Finally, the kinetics of the exposure has also revealed that the $m$-ZnTCPP response was twice as fast as $p$-ZnTCPP.

Overall, the $m$-ZnTCPP/TiO$_2$ films exhibited better gas-sensing properties than those based on $p$-ZnTCPP as a consequence of the different position of the peripheral carboxylic groups, whose specific anchoring to the titania surface leads to a different aggregation state in the solid film.

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References


32. A. D. F. Dunbar, T. H. Richardson, A. J. McNaughton, J. Hutchinson, and C. A.
Supporting Information

**Figure S1.** Specular reflectance FT–IR spectrum of a columnar TiO$_2$ film.
Figure S2. Pre-exposure (solid line), exposure (dashed line) and difference (dashed dotted line) spectra of m-ZnTCPP/TiO$_2$ (left) and p-ZnTCPP/TiO$_2$ (right) composite films upon exposure to acetone, acetonitrile, butylamine, chloroform, ethanol and tetrahydrofuran.
Free-base carboxyphenyl porphyrin films using a TiO$_2$ columnar matrix: characterization and application as NO$_2$ sensors.

1. Introduction

Porphyrrins are a family of compounds with chemical and physical properties that make them interesting for new technologies such as solar cells, photodynamic therapies or gas sensors. In the latter field, researchers have been investigating during the last decades the capabilities of porphyrins to detect a variety of gases. Porphyrins 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.

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 NO$_2$ and some free-base porphyrins is well documented in the literature, producing strong changes in the absorption spectrum that can be easily monitored. 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 NO$_2$, either modifying the technique of deposition or combining the sensing material with host molecules, with outstanding results. 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.

Anchoring of porphyrin molecules to TiO$_2$ by adding carboxylic acid groups to their structure has given great results in terms of film fabrication and its applicability. Originally developed by solar cell researchers, the chemical binding to
TiO\textsubscript{2} 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. The elaboration of glancing angle physical deposition (GAPVD) films has attracted our attention in the last few years as their properties are nearly ideal for the construction of optical sensing devices. These films feature TiO\textsubscript{2} 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.\textsuperscript{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,\textsuperscript{7,12} and the position itself of the peripheral groups may determine different states and types of aggregation.\textsuperscript{9} We have previously reported the effect of the position of carboxylic substituents on the anchoring to titania substrates,\textsuperscript{13} finding that porphyrins bound to TiO\textsubscript{2} columnar films by four points have little tendency to form aggregates and that their sensing performance towards volatile organic compounds (VOCs) is better than films made with porphyrins anchored by only one or two points.

Here we evaluate the anchoring effect on free-base carboxyphenyl porphyrin films using TiO\textsubscript{2} microstructured columns as host matrix and its influence on NO\textsubscript{2} sensing. Three different free-base porphyrins have been used for this purpose: 5-(4-carboxyphenyl)10,15,20-triphenyl-21\textsubscript{H},23\textsubscript{H}-porphyrin (MCTPP, Fig. 1A), 5,10,15,20-tetrakis(4-carboxyphenyl)-21\textsubscript{H},23\textsubscript{H}-porphyrin (\textit{p}-TCPP, Fig. 1B) and 5,10,15,20-tetrakis(3-carboxyphenyl)-21\textsubscript{H},23\textsubscript{H}-porphyrin (\textit{m}-TCPP, Fig. 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 NO\textsubscript{2} have been investigated by analyzing the responses of the composite films upon their exposure to different concentrations of the toxic gas.
2. Material and methods

2.1. Porphyrins and reagents

MCTPP, \( p \)-TCP and \( m \)-TCP were purchased from Frontier Scientific, Inc. and used as received. All reagents were purchased from Sigma-Aldrich and used without further purification.

2.2. Film preparation

We prepared transparent and amorphous \( \text{TiO}_2 \) columnar films by the GAPVD technique at an angle of deposition of 70° with respect to the evaporation source. The angle formed by the columns and the substrate was approximately 60°, with a film thickness of approximately 350 nm exhibiting an elevated porosity (total pore volume of 49 %) with void apertures on the surface in the form of mesopores (pore diameter > 2 nm), that also determines a relatively low refractive index value, that was found to be 1.79.14 Further details regarding film preparation, SEM images and structural information can be found elsewhere.11 The high porosity of the films would
allow the accessibility of porphyrins during the composite film preparation and NO$_2$ during the gas sensing experiments. For specular reflectance Fourier transform infrared (FT–IR) spectroscopy, the films were deposited on gold-coated silicon substrates. Films for UV-visible spectroscopy were prepared on glass substrates. Binding of porphyrins to the TiO$_2$ films was performed by immersion of the substrates in a 5*10$^{-4}$ M MeOH solution of the dye for 2 h. After this, the films were rinsed with MeOH to remove physisorbed dye molecules and dried at room temperature (~293 K) under a dry N$_2$ stream.

2.3. Infrared and UV-visible spectroscopy

We studied the binding of the carboxylic porphyrins to TiO$_2$ through specular reflectance FT–IR spectroscopy using a Jasco FT/IR–6200 spectrometer. The specular reflectance FT–IR spectra for the porphyrins were measured neat (by casting on silicon substrates) and bound to the TiO$_2$ thin films.

UV-visible spectra of the porphyrins were recorded in MeOH solution using an Ocean Optics USB4000 spectrophotometer.

2.4. Gas exposure

We placed the porphyrin films in a gas testing system for the exposure to NO$_2$. This system consisted of a purpose-built gas chamber with a gas inlet and an outlet, connectors for two optical fibers and a Peltier heating-cooling device. Two Bronkhorst F-201FV mass flow controllers were used to control the flow rates of gases. The chamber was connected to an Ocean Optics USB4000 optical fiber spectrophotometer to record the UV-vis spectrum of the films during their exposure to NO$_2$.

We used two gas cylinders to obtain the desired NO$_2$ concentration, one containing 500 ppm NO$_2$ in dry nitrogen and another containing pure dry nitrogen. Each of the cylinders was connected to a mass flow controller and after this both gas lines were linked together and directed into the chamber. Precise NO$_2$ concentrations were obtained by modifying the flow from each of the gas cylinders and hence diluting 500 ppm NO$_2$ with dry nitrogen.

Before NO$_2$ exposure, the chamber was flushed with dry N$_2$ to ensure an inert internal atmosphere, thus preventing the contamination the samples. Then, we introduced the corresponding sample into the gas chamber while keeping a constant dry N$_2$ flow through the gas inlet to allow complete desorption of possible contaminating gases that could be adsorbed on the sample. For the gas exposure phase, the gas mixture containing the desired NO$_2$ concentration was introduced in the chamber until the porphyrin was fully saturated. In all cases the samples were exposed at room temperature (~293 K). The recovery phase consisted in the introduction of dry N$_2$ in the chamber while simultaneously heating the sample with
the Peltier device at elevated temperature (~373 K) to desorb NO₂ molecules from the film.

3. Results and discussion

3.1. Composite porphyrin/TiO₂ films characterization

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 (Fig. 2). Once bound to TiO₂, each porphyrin experienced different changes in their spectra. The Soret band in MCTPP/TiO₂ films band was strongly broadened (full width at half-maximum: 40.5 nm) and blue-shifted (8 nm) with respect to the solution spectrum (Fig. 2A). Besides the broadening of the Soret band, its shape revealed the contribution of two peaks, indicating the presence of, at least, two species in the film. The main peak, located at 406 nm, would be generated by the formation of H aggregates of porphyrin molecules. The secondary peak, less intense, is represented by a shoulder around 417 nm, and would correspond to the monomeric form of the porphyrin. When bound to TiO₂, p-TCPP showed similar behavior as MCTPP/TiO₂ films, although slightly less broadened (full width at half-maximum: 38 nm) and blue-shifted (5 nm) (Fig. 2B). The shape of the Soret band also indicated the presence of more than one species in the film. However, in this case the main peak was less blue-shifted than that of MCTPP in film, indicating a higher contribution of the monomeric form of the porphyrin to the spectrum. The spectrum of m-TCPP bound to TiO₂ showed much more similarity to that obtained from its solution, with a narrower Soret band (full width at half-maximum: 30.5) and a main peak at 415.5 nm, hence practically nonshifted (Fig. 2C). Nevertheless, a small shoulder appeared around 400 nm, corresponding to the formation of a certain number of H aggregates.
Film stability was accomplished by recording composite films spectra every day or every few days until 20 days from the preparation of the films (Fig. 3). During this time, except during their UV-vis spectra measurement, samples were stored in the dark and preserved from contact with any contaminating gases. The effect of time on all porphyrin films had two main results. First, all films featured a loss of intensity in their absorbance, which can be attributed to the formation of large porphyrin clusters. Second, there was a decrease in the contribution of the lower wavelength peak to the film spectrum in all three cases, probably due to the little stability of H aggregates, which led to a progressive red shift of the Soret band over time. In MCTPP and p-TCPP films, the shape of the spectra after 20 days showed a change in the position of the main peak to a wavelength of 415.5 nm and 419 nm, respectively. The spectrum of m-TCPP after 20 days was modified as explained, but the main peak was still primarily composed by the monomeric species of the porphyrin as in the initial spectrum and the overall change observed in the film was smaller than in the cases of MCTPP and p-TCPP films.
Fig. 3. Temporal evolution of the UV-vis absorption spectra of MCTPP/TiO$_2$, $p$-TCPP/TiO$_2$ and $m$-TCPP/TiO$_2$ composite films over 20 days. The spectra of the porphyrins in MeOH solution is included for comparison. All spectra have been normalized with respect to their corresponding initial spectrum.

Further information about film stability over time was obtained through the analysis of the spectral changes experienced by the composite films after a long period of time (Fig. S1 in the Supporting Information). Seven months after their preparation, MCTPP and $p$-TCPP films spectra showed a flat line without any trace of their respective Soret bands. This effect may be attributed to the extended formation of porphyrin clusters leading to an uncolored film. However, $m$-TCPP film spectrum remained similar to that obtained 7 months before, indicating once again that composite films made with this porphyrin are highly stable.

The differences in the aggregation state and stability of the porphyrins in film can be explained through their different binding to the TiO$_2$ matrix. MCTPP would be anchored by its only carboxylic group, which leads to a flexible union between porphyrin and TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ matrix while lying flat to the surface,
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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 TiO$_2$ and their influence on aggregation was obtained by the analysis of their IR spectra. Specular reflectance FT–IR spectra of $m$-TCP and p-TCPP porphyrins neat and bound to TiO$_2$ are shown in Fig. 4. The binding interaction between the porphyrin and the metal oxide surface is revealed by the comparison of changes in the region of the carbonyl group in the FT–IR spectra. Neat samples of $m$-TCP showed strong bands at 1725 cm$^{-1}$ and 1286 cm$^{-1}$ which are characteristic of the $\nu$ (C=O) stretch and the $\nu$ (C–O) stretch of the carboxylic acid groups, respectively. In the case of p-TCPP, where the –COOH groups are situated in the plane of the tetrapyrrole macrocycle, the extensive hydrogen bonding of the carboxylic acid groups resulted in a shift to lower frequency of the $\nu$ (C=O) stretch at 1595 cm$^{-1}$ and a shift to higher frequency of the $\nu$ (C–O) stretch at 1400 cm$^{-1}$.

![Fig. 4. Specular reflectance FT–IR spectra of $m$-TCP and p-TCPP neat (by casting on silicon substrates) and bound to TiO$_2$.](image)

Binding of $m$-TCP to TiO$_2$ resulted in the disappearance of the $\nu$ (C=O) and $\nu$ (C–O) stretching modes and the appearance of new bands in the 1395–1430 cm$^{-1}$ and 1530–1560 cm$^{-1}$ regions, corresponding to the symmetric and asymmetric $\nu$ (CO$_2$)
stretches, respectively. A strong and broad band around 1635 cm\(^{-1}\) generated by the free TiO\(_2\) molecules of the columnar film hindered partially the bands corresponding to the asymmetric \(\nu\) (CO\(_2\)) stretch, but these were still evident. In the case of \(p\)-TCPP/TiO\(_2\), the bands generated by the C=O and C–O stretching modes were still partially present with a slight broadening of the latter. In this case, the appearance of the band corresponding to the symmetric \(\nu\) (CO\(_2\)) stretch is not so evident due to overlapping with the remaining \(\nu\) (C–O) stretch band, although its broadening indicates the contribution of the former. Moreover, the changes in the 1500–1750 cm\(^{-1}\) region, where the asymmetric \(\nu\) (CO\(_2\)) stretch band was expected to appear, were hindered by the presence of the band corresponding to the free TiO\(_2\) molecules.

Chemical binding of carboxylic acids to TiO\(_2\) colloidal films has been associated with the disappearance of the bands corresponding to the \(\nu\) (C=O) and \(\nu\) (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 \(\nu\) (CO\(_2\)) stretches respectively.\(^\text{10}\) These spectral changes have been found to be compatible with chelating and/or bidentate binding modes of the carboxylate groups on the TiO\(_2\) surface.\(^\text{10,16–19}\)

The analysis of the IR spectrum of \(m\)-TCPP/TiO\(_2\) revealed that this was consistent with the absence of free carboxylic acid groups, given that C=O and C–O stretching modes disappeared completely. This suggests a planar situation of the porphyrin macrocycle with respect to the titania surface in which all carboxyl groups are bound to the TiO\(_2\).\(^\text{10}\) However, in the case of \(p\)-TCPP/TiO\(_2\), the stretching modes corresponding to C=O and C–O disappeared only partially, indicating the presence of free carboxylic acid groups coexisting with carboxylate groups bound to TiO\(_2\). As a result of this, and due to the planar structure of the \(para\) substituted \(p\)-TCPPs, it can be expected that they are bound only by one or two of its four carboxyl groups to the metal oxide surface resulting in a perpendicular orientation of the molecule with respect to the surface that allows them to interact (face to face) with other molecules, causing aggregation.\(^\text{10,20}\)

From these results we can infer that MCTPP will be bound to the TiO\(_2\) through the same binding modes as \(p\)-TCPP. Although study its IR spectrum was not possible, the molecular structure of MCTPP, with only one carboxyl group, can only be bound to TiO\(_2\) by one anchoring point. Hence, and due to its planar structure, MCTPP molecules are likely to be perpendicularly oriented with respect to the surface, which allows the formation of face to face aggregates.

### 3.2. \(\text{NO}_2\) detection

MCTPP/TiO\(_2\), \(p\)-TCPP/TiO\(_2\) and \(m\)-TCPP/TiO\(_2\) composite films were exposed to 500 ppm \(\text{NO}_2\) to assess their sensing performance. The exposure of the films to the toxic gas resulted in the disappearance of the typical Soret band of the porphyrins
and the appearance of a new band around 435 nm (Fig. 5), which is consistent with results from other authors using different free-base porphyrins. These spectral changes are well documented and, given that porphyrins are electron-rich systems and NO$_2$ is a strong oxidizing agent, a charge transfer process in the form of oxidation is the most probable mechanism for such behavior. 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 N$_2$ stream, which makes them good candidates for single-use NO$_2$ sensors. Other recovery strategies are a subject of further research.

![Figure 5](image-url)

**Fig. 5.** Pre-exposure (solid line) and exposure (dashed line) spectra of MCTPP/TiO$_2$, p-TCPP/TiO$_2$, and m-TCPP/TiO$_2$ composite films upon exposure to 500 ppm NO$_2$.

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 NO$_2$ (Fig. 6). All porphyrins featured fast changes with similar response shapes. After the signal was stabilized, we proceeded to the recovery phase with N$_2$ while heating the samples, which led to a partial reversibility as indicated before. To quantify the speed of response, we calculated $t_{50}$, which is the time taken for the absorbance to reach 50% of its maximum value. The obtained $t_{50}$ values for MCTPP/TiO$_2$, p-TCPP/TiO$_2$, and m-TCPP/TiO$_2$ composite films were 31, 30, and 33 sec, respectively, confirming the fast response of all films.
Fig. 6. Kinetics of the exposure of MCTPP/TiO$_2$, p-TCPP/TiO$_2$ and m-TCPP/TiO$_2$ composite films to 500 ppm NO$_2$ measured at 447, 445 and 442 nm, respectively.

The information obtained from the analysis of the spectral changes and the speed of response indicated that films made with MCTPP, p-TCPP and m-TCPP worked similarly upon their exposure to NO$_2$. Therefore, there is no clear evidence that the different anchoring geometries of our porphyrins have a strong influence on the sensing capabilities of the composite films. However, the less aggregated state and much better stability over time achieved by m-TCPP once bound to TiO$_2$ suggests this as the best candidate among our set of porphyrins to be used as NO$_2$ sensor. Hence, from this point on we will analyze the spectral responses of m-TCPP/TiO$_2$ composite films towards low concentrations of NO$_2$ to further characterize its sensing performance.

In order to study the concentration dependence of the response of m-TCPP/TiO$_2$ composite films to NO$_2$, we exposed the samples to 25, 33, 50 and 100 ppm NO$_2$, obtained by diluting a gas stream containing 500 ppm NO$_2$ with another N$_2$ stream. The exposure to increasing concentrations of NO$_2$ led to increasing changes in the films spectra, indicating a concentration-dependent behavior of the system (Fig. 7). The values of magnitude of response, measured as the increment of absorbance at the maximum change wavelength and corresponding to 25, 33, 50 and 100 ppm NO$_2$ were 0.273, 0.315, 0.372 and 0.433, respectively, confirming that the response was intensified as the concentration of NO$_2$ was increased. We also calculated $t_{50}$ to account for different speeds of response after the exposure to each of the gas concentrations. The obtained $t_{50}$ values for the exposure of the composite films to 25, 33, 50 and 100 ppm NO$_2$ were 1100, 1040, 620 and 420 sec, respectively. These values confirm that the response, although slow at low concentrations, becomes faster when more NO$_2$ molecules are available, further confirming a concentration-dependent...
behavior of m-TCPP/TiO₂ composite films. These results suggest that the system is appropriate to be used for quantification purposes through the performance of a simple calibration for the desired range of concentrations.

![Graph](image)

**Fig. 7.** Kinetics of the exposure of m-TCPP/TiO₂ composite films to 25, 33, 50 and 100 ppm NO₂ at a wavelength of 442 nm.

### 4. Conclusions

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 have the advantage of being easy to prepare with respect to other deposition techniques.

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/TiO$_2$ composite films to low concentrations of NO$_2$ 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 NO$_2$ sensor.

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References

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Supporting Information

Fig. S1. UV-vis absorption spectra of MCTPP/TiO$_2$, $p$-TCPP/TiO$_2$ and $m$-TCPP/TiO$_2$ composite films after preparation (solid black line) and seven months later (dashed black line). The spectra of the porphyrins in MeOH solution is included for comparison.
CAPÍTULO 7

Optical detection of amine vapors using ZnTriad porphyrin thin films

1. Introduction

The detection of amines is of high interest given the amount of processes in which they take part. For instance, some biogenic amines, including histamine, putrescine and cadaverine, appear as bacterial metabolic products of rotting food, especially in fish and meat, allowing their use as food freshness indicator.\textsuperscript{1-2} The presence of unusual concentrations of biogenic amines can also help in the diagnosis of certain illnesses, such as bacterial vaginosis.\textsuperscript{3} Another example of process in which amines take part is the industrial production of polymers, dyes, pharmaceuticals and other chemicals, in this case as reaction intermediates. Some of them, mainly of aromatic nature as aniline, are proven to be toxic and need to be controlled to ensure a healthy industrial environment.\textsuperscript{4}

Detection strategies based on gas chromatography or high-performance liquid chromatography have proved to give good results but are complex to implement and require a lot of processing time.\textsuperscript{5} Sensors based on electrochemical or optical devices have been researched over the last decades with good outcome.\textsuperscript{6,7} These techniques are non-destructive and relatively straightforward, and have the added advantage of being less expensive than the separation procedures.

Metalloporphyrins have shown to be excellent candidates for the detection of amines, among other volatile organic compounds (VOCs), given their ability to interact with metal-ligating vapors.\textsuperscript{8} In particular, metal-derivatives of tetraphenylporphyrin (TPP) have been used for amine sensing with satisfactory results.\textsuperscript{9,10} The flat and open geometry of TPPs allows gas molecules to easily access the porphyrin core and interact with its $\pi$ electron system, modifying the porphyrin spectrum and making it useful for optical gas-sensing. However, intermolecular $\pi-\pi$ interactions between porphyrin rings usually lead to an aggregated state that, in general, is detrimental for gas-sensing applications as it prevents the gas-porphyrin interaction.\textsuperscript{11} The absence of large peripheral substituents, which is the case of TPPs, facilitates porphyrin aggregation when the molecules are deposited on a film,\textsuperscript{12-16} limiting their sensing abilities.

Anti-aggregation strategies for this kind of molecules have been generally based on preventing interaction between porphyrins by separating them in some way. Apart from the addition of bulky peripheral groups to the TPP ring, these strategies
include the use of host molecules such as calixarenes,\textsuperscript{17-19} porous substrates such as silica gel,\textsuperscript{9} or chemical binding of the porphyrin to a specific substrate such as TiO\textsubscript{2} thin films.\textsuperscript{20-22}

An alternative approach to prevent the aggregation while using simple deposition methods, is the creation of multiporphyrin structures that avoid porphyrin contact through steric hindrance. Recently, a new methodology for the preparation of tripodal metalloporphythin systems has been developed.\textsuperscript{23} These molecules are based on three metalated TPPs linked through a 2-(hydroxymethyl)-s-methylpropane-1,3-diol unit, which separates the tetrapyrroles enough to allow access of small molecules, while keeping the photophysical properties of the system similar to the monomeric ones.\textsuperscript{24} On one hand, the geometry of these molecules distributes the tetrapyrroles in such a way that intramolecular aggregation is avoided, while intermolecular interactions are possibly hindered. On the other hand, the specific separation between tetrapyrroles within the tripodal porphyrin may act as a filter to incoming gas molecules, which might lead to the selective detection of analytes according to their size and shape. Similar uses of multiporphyrin systems for gas-sensing purposes can be found in the literature.\textsuperscript{10,25}

In this work, we used 1,3-di[5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin]-2-(5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin)-2-methylpropane Zn(II) (ZnTriad, Fig. 1A) to detect amines through UV-vis spectroscopy. We also compared ZnTriad to its single unit, Zn(II) 5,10,15,20-tetraphenylporphyrin (ZnTPP, Fig. 1B) to assess the influence of the branched structure on molecular aggregation and sensing capabilities. The films were prepared by sping coating on glass. In order to test if the geometry of ZnTriad facilitates the selective detection of amines regarding their size and shape, we chose a total of five primary amines (Fig. 1C), being three of them linear or one-dimensional with increasing length (propylamine, butylamine and hexylamine), one planar or two-dimensional (aniline) and one three-dimensional (tert-butylamine). Our hypotheses are that (i) the multiporphyrin geometry can avoid molecule aggregation when deposited on solid substrates, improving the sensing capabilities of the system, and that (ii) the specific separation among tetrapyrroles in the tripodal porphyrin may lead to selective responses towards different sizes and shapes of the amines.
Fig. 1. Molecular structures of (A) 1,3-di[5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin]-2-(5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin)-2-methylpropane Zn(II) (ZnTriad), (B) Zn(II) 5,10,15,20-tetraphenylporphyrin (ZnTPP), and (C) the studied amines: aniline, tert-butylamine, hexylamine, butylamine and propylamine (top to bottom, left to right).

2. Material and methods

2.1. Porphyrin and reagents

ZnTriad synthetic procedure is described elsewhere. ZnTPP was purchased from Frontier Scientific Europe Ltd. and used as received. All reagents were purchased from Sigma-Aldrich and used without further purification.

2.2. Film preparation

Porphyrin films were prepared by spin-coating a 5 x 10^-5 M chloroform solution of ZnTriad or ZnTPP on approximately 4 cm² cut-to-size glass slides (Menzel-Glaser microscope slides). Spin-coater was programmed to spin at 500 rpm for 5 sec, followed by 2 sec at 2000 rpm and a final 30 sec phase at 4000 rpm. Samples were then heated at 100 °C to desorb any solvent trapped in the film.

2.3. Gas exposure

We placed the porphyrin films in a gas testing system for the exposure to amine vapors. This system consisted of a purpose-built gas chamber with a gas inlet and an outlet, connectors for two optical fibers and a Peltier heating-cooling device. Two Bronkhorst F-201FV mass flow controllers were used to control the flow rates of
Optical detection of amine vapors using ZnTriad porphyrin thin films

The chamber was connected to an Ocean Optics USB4000 optical fiber spectrophotometer to record the UV-vis spectrum of the films during their exposure to amines.

We obtained the gaseous amines by bubbling dry nitrogen through a bottle containing a mixture of the desired liquid amine and dodecane immersed in a temperature-controlled water bath. Dodecane was used to dilute the amines and hence modify their respective vapor pressures to obtain the desired concentration in the gaseous phase. The alkane did not alter in any way the spectra of the films. In order to obtain the exact desired amine concentration, we diluted the amine–N₂ gas stream with another pure N₂ gas stream, and calculated the final concentration through their vapor pressure in the diluted dodecane solution at the corresponding temperature and the dilution factor with pure N₂ in the carrying gas. Similar procedures for the generation of low concentrations of VOCs can be found in the literature.

Before the amine exposure, the chamber was flushed with dry N₂ to ensure an inert internal atmosphere, hence preventing the contamination of the samples. Then, we introduced the corresponding sample into the gas chamber while keeping a constant dry N₂ flow through the gas inlet to allow complete desorption of possible contaminating gases that could be adsorbed on the sample. For the gas exposure phase, the gas mixture containing the desired amine was introduced in the chamber until the porphyrin was fully saturated. In all cases the samples were exposed at room temperature (~293 K). The recovery phase consisted in the introduction of dry N₂ in the chamber while simultaneously heating the sample with the Peltier device at elevated temperature (~373 K) to allow complete desorption of the amines from the film.

3. Results and discussion

3.1. Film characterization and sensing capabilities

The UV-vis spectra of ZnTriad and ZnTPP in chloroform solution showed their monomeric forms, with their Soret band peaking at 422 nm and 419 nm and full widths at half-maximum of 14 nm and 11 nm, respectively (Fig. 2). Apart from a slight red-shift (3 nm) and broadening (3 nm at half-maximum) of ZnTriad spectrum with respect to that of ZnTPP, the spectral shapes of both porphyrins were very similar. Therefore, it can be assumed that the spectral behavior of the three tetrapyrrolic rings in ZnTriad is the same as if they were isolated. However, it has been reported that the molar absorption coefficient for the Soret band per porphyrin in the free-base triad is twice of its monomer, probably due to a decrease in the symmetry, which may be advantageous for optical sensing applications owing to an
When deposited as thin films ZnTriad appeared slightly broadened (full width at half-maximum: 24 nm) and 11 nm red-shifted with respect to the solution (Fig. 2A), while ZnTPP films were more broadened (full width at half-maximum: 26 nm for the film) and featured a 15 nm red-shift (Fig. 2B).

The observed red-shift and broadening of the Soret band in both porphyrins when deposited as films indicates that a certain number of molecules were forming J-aggregates as a result of the strong intermolecular π-π interaction that can be found in this kind of molecules.\textsuperscript{26-28} However, the amount of spectral shift and broadening featured by ZnTriad films was lower than in the case of ZnTPP, that rapidly develops to further aggregation and clustering revealing a very different tendency towards aggregation. The planar geometry of ZnTPP and the lack of peripheral substituents that could hamper porphyrin interaction explain its highly aggregated state on films. ZnTriad, as a tripodal porphyrin, is formed by three different ZnTPP units linked together. Its three tetrapyrroles are kept separate owing to the molecule geometry, and hence intramolecular aggregation is not possible. Intermolecular interaction is
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still possible, causing a certain number of aggregates that explain the modifications observed in ZnTriad films with respect to solution. However, its three-dimensional structure, as opposed to planar ZnTPP, hinders long-range interaction between macrocycles and thus strong aggregation. As a result of this, the amount of aggregation using ZnTriad is considerably lower than with ZnTPP.

Stability of the films was accomplished by the study of their evolution over time. ZnTriad films remained unaltered and with the same UV-vis spectrum up to one month after their preparation (data not shown). In contrast, ZnTPP featured a fast aggregation followed by a clustering process that led to an intense decrease of the Soret band after a short period of time (Fig. 2B). According to the aggregation kinetics, the Soret band absorbance diminished to 50 % of its initial value after 15 min (Fig. S1). Cluster formation and loss of coloration of the film caused by the molecules stacking together and creating voids in the film was noticeable with the naked eye. Detailed spectral temporal evolution can be seen in Fig. S2. As a result from this fast aggregation process, ZnTPP films were not stable enough to be used even in short-term experiments, and therefore unusable for the creation of gas sensitive films. Similar aggregation was found in films made on hydrophobic glass (data not shown). These results reinforce the interest of using a multiporphyrin system such as ZnTriad for the optical detection of gases.

The study of sensitivity, reversibility and repeatability was accomplished by exposing ZnTriad films to butylamine vapors. This amine has proved to induce large spectral changes on different porphyrins\textsuperscript{7,10,17,22,29}, and therefore is a good candidate to test the system response to amines. Upon exposure to 90 ppm butylamine, ZnTriad film Soret band featured a 3 nm shift to higher wavelength and an increase of its maximum absorbance (Fig. 3). This behavior is similar to the observed in single porphyrins\textsuperscript{21} and suggests that the tripodal organization of ZnTriad is not detrimental for gas sensing purposes.

![Fig. 3. Pre-exposure (solid line), exposure (dashed line) and difference (dotted line) spectra of a ZnTriad film upon exposure to 90 ppm butylamine.](image-url)
After three consecutive cycles of exposure to 90 ppm butylamine and recovery with N\textsubscript{2}, ZnTriad films showed intense and fast responses, complete reversibility and excellent repeatability among cycles (Fig. 4), which further supports that our porphyrin is a good candidate for the detection of amines.

![Fig. 4](image)

**Fig. 4.** Kinetics of the exposure of a ZnTriad film to 90 ppm butylamine gas at a wavelength of 440 nm.

To assess the concentration dependence of the response, ZnTriad films were exposed to six concentrations of butylamine ranging from 90 to 3200 ppm. The results of magnitude of response, measured as the increment of absorbance at the maximum change wavelength and corresponding to 90, 435, 800, 1600, 2400 and 3200 ppm were of 0.0042, 0.0053, 0.0060, 0.0066, 0.0070 and 0.0072, respectively, indicating that the response was intensified as the concentration of butylamine was increased. Such behavior suggests that the system is appropriate to be used for quantification purposes through the performance of a simple calibration for the desired range of concentrations.

Further characterization of the concentration dependence was obtained by applying an isotherm model. The Langmuir adsorption isotherm\textsuperscript{30} can be used for the study of the adsorption of different types of molecules onto different materials,\textsuperscript{21,31-33} and in our case is a helpful tool to describe the adsorption/desorption equilibrium of the gaseous amine molecules onto the porphyrin film solid surface. The model is usually expressed by:

$$\frac{n_{\text{ads}}}{N_s} = \frac{\lambda c}{1 + \lambda c} \quad \text{(eq. 1)}$$

where \(n_{\text{ads}}\) is the number of gas molecules adsorbed (which is proportional to the change in Soret band absorbance, \(\Delta \text{Absorbance}\)), \(N_s\) is the number of adsorption sites, \(\lambda\) is a constant relating to the adsorbability of the gas and \(c\) is the concentration of the gas, [Butylamine]. Rearrangement of eq. 1 leads to the linear form of the Langmuir
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adsorption isotherm:

\[
\left( \frac{c}{n_{\text{ads}}} \right) = \left( \frac{c}{N_S} \right) + \left( \frac{1}{N_S \lambda} \right) \quad \text{(eq. 2)}
\]

Thus, the plot of \( c/n_{\text{ads}} \) versus \( c \) should generate a straight line if the data points follow the Langmuir model.

In our case, the plot of \( c/\Delta \text{Absorbance} \) vs. \( c \) fitted a straight line (Fig. 5), indicating that the conditions for the Langmuir adsorption model are satisfied. Therefore, and according to the assumptions of this model, it can be concluded that the activation energy of adsorption is the same for all binding sites in the porphyrin film, that there are a fixed number of localized surface sites present on the surface and that butylamine molecules striking a surface site that is already occupied do not adsorb onto that particular site.

![Fig. 5. Langmuir adsorption plot for ZnTriad films upon exposure to butylamine gas ranging from 90 to 3200 ppm.](image)

A higher concentration range was also tested with similar results, showing that the system can be used to quantitate at least up to 57000 ppm butylamine (Fig. S3). The application of the Langmuir adsorption model to this range of concentrations resulted in a good fitting to a straight line (\( R^2 = 0.99633 \), Fig. S4), indicating that the system follows the Langmuir model also at high concentrations.

3.2. Shape selective detection of amines

ZnTriad films were exposed to 90 ppm aniline, tert-butyamine, hexylamine, butylamine and propylamine to assess the potential shape-selective detection ability of our system. The analysis of the sensing performance was accomplished through the study of the changes undergone by the UV-vis spectra of the porphyrin films upon their exposure to the corresponding amine. To provide an easier way to follow these changes, we examined the absolute value of the difference spectra, obtained by...
subtracting the non-exposed spectrum to the exposed one in each case. Once in contact with the amines, ZnTriad films featured important changes in their UV-vis spectra, which was evident in their corresponding difference spectra (Fig. 3 and 6). In all cases the exposed spectra was increased and shifted to higher wavelengths with respect to the non-exposed one. This caused the difference spectra to be formed by two bands of similar shape at approximately 420 and 445 nm, but with different relative heights and intensity that can be used to differentiate the amines. A closer analysis of the difference spectra reveals that the highest changes were obtained in the case of the linear amines, while the exposure to aniline and tert-butylamine led to smaller but evident changes. In those cases where the changes were of similar intensity, the relative heights of the bands in the difference spectra can help to the identification of the amine. For example, hexylamine and butylamine provoked a similar change in intensity, but the relative height of the band around 445 nm with respect to that situated at 420 nm is considerably higher in the case of hexylamine.

Fig. 6. Pre-exposure (solid line), exposure (dashed line) and difference (dotted line) spectra of a ZnTriad film upon exposure to 90 ppm aniline, tert-butylamine, hexylamine and propilamine.

A quantification of the spectral response of ZnTriad to each of the amines, defined as change fraction, was obtained by dividing the area of the difference spectrum by the area of the unexposed spectrum (Fig. 7). This procedure results in a unique value that reflects the amount of change induced to the porphyrin by the amine, independently of the amount of porphyrin in the film. Although somewhat simplistic, this value allows us to compare directly all responses at a glance. The change fraction values indicate that the highest responses occurred after the exposure to linear amines, as could be expected given the results from the analysis of the difference spectra. Aniline was the amine which induced least change to the porphyrin films, followed by tert-butylamine. Hexylamine, butylamine and
propylamine exposure led to change fractions twice as high as the corresponding to aniline. These results suggest an influence of the shape and size of the amine on the sensing process. The spectral changes induced on metalloporphyrins upon their exposure to certain compounds depend on the accessibility to the porphyrin coordination sites, located in the central ring of the macrocycle.\textsuperscript{34,35} Aggregation in porphyrin films is generally detrimental for gas sensing purposes\textsuperscript{11,22} as it reduces available sites for incoming gas molecules. In the case of a single monomeric porphyrin there are two sites for axial ligation, each corresponding to one of both sides of the planar macrocycle. When aggregation occurs, dye molecules stack one over another, blocking the access to gas molecules. In extremely aggregated systems, as is the case of ZnTPP, it results in a pile of molecules where only the first and the last porphyrin (i.e. the top and the bottom of the pile) are easily accessible to gases. Owing to the tripodal geometry of ZnTriad, this effect is greatly avoided and thus its sensing capabilities are more than satisfactory. Moreover, the three-dimensional structure of this multiporphyrin can also act as a filter to gas molecules. The distance from each of the monomers to the adjacent one may limit the accessibility into the multiporphyrin inner space according to the size of the incoming molecule. According to this assumption, big molecules will induce less change than small ones due to their limited access to ligation sites. This is consistent with the resulting change fraction values, as we can assume that linear amines (hexylamine and butylamine) can enter more easily in ZnTriad inner space than planar (aniline) or three-dimensional (\textit{tert}-butylamine) amines.

![Fig. 7. Change fraction values obtained from the exposure of ZnTriad films to 90 ppm aniline, \textit{tert}-butylamine, hexylamine, butylamine and propylamine.](image)

In order to show graphically in a single image both the amount of spectral change and the wavelengths where it happens, we created identification patterns for the exposure to each amine (Fig. 8). This procedure has been successfully used in recent studies to create fingerprints for VOCs\textsuperscript{21} and to compare the sensing capabilities of two similar porphyrins.\textsuperscript{22} The resulting patterns summarize the behavior of the
sensing system, representing as a color image the intensity and distribution of the spectral change obtained from the difference spectra. This way, every column in the image shows the changes experienced by the films after their exposure to each of the amines, allowing direct comparison among all of them. Further details regarding the procedure for obtaining these identification patterns can be found elsewhere.\textsuperscript{21} A quick look at the image in Fig 8 is enough to identify two groups of patterns according to the color scale. Hexylamine, butylamine and propylamine are characterized by strong dark blue bands, corresponding to maximum change points, while aniline and tert-butylamine do not show this color. A closer analysis reveals that aniline and tert-butylamine are also easily differentiated by the presence of a light blue band in the latter. The discrimination of the linear amines is not so straightforward as they all three exhibit maximum change points in similar regions, but the combination of intensity and position of their corresponding color bands provides a unique pattern in each case that can be used for identification purposes.

Given the selectivity achieved with molecules within the same chemical group, ZnTriad would be an excellent choice for its inclusion in sensor arrays. Other multiporphyrin molecules have been used for chemical sensing by other authors as part of porphyrin arrays,\textsuperscript{10,25} taking advantage of their abilities towards the detection of compounds within a particular chemical group. Testing our system for the detection and discrimination of secondary and tertiary amines according to their size and shape is a subject of future research. Together with the results obtained in this study with primary amines, it will provide valuable information for the integration of ZnTriad in sensor arrays.

![Fig. 8. Identification patterns corresponding to the exposure of ZnTriad films to 90 ppm aniline, tert-butylamine, hexylamine, butylamine and propylamine. Color scale goes from red to blue, where red indicates no change between pre-exposure and exposure spectra and blue is the highest change detected in all cases.](image)

Sensor kinetics was studied by recording ZnTriad films absorbance at the
wavelength of maximum change during their exposure to 90 ppm of each amine. As a result of the interaction with the analytes, film absorbance at the selected wavelength increased in all cases. The analysis of kinetics was accomplished through the parameter of response time, $t_{50}$, which is the time taken for the absorbance to reach the 50% of its total maximum change and represents the speed of response in each case. Mean $t_{50}$ corresponding to three different cycles of exposure-recovery to each of the amines ranged from 41 to 78 sec (Fig. 9). The fastest times were obtained after the exposure to hexylamine, butylamine and propylamine. Aniline and tert-butylamine responses were considerably slower, suggesting hindered amine diffusion to the porphyrin active sites that may be caused by the bigger size or particular shape of these amines.

![Fig. 9](image.png)

**Fig. 9.** Mean $t_{50}$ values corresponding to the exposure of ZnTriad films to 90 ppm aniline, tert-butylamine, hexylamine, butylamine and propylamine. Error bars are SE.

The results from change fraction, identification patterns and sensor kinetics indicate a more than probable influence of the shape or size of amines on the sensor behavior. Linear amines induced, in all cases, more intense and faster changes on ZnTriad films spectra than those with planar or three-dimensional structure. The amine with planar geometry, aniline, produced the smallest and slowest change, followed by the three-dimensional tert-butylamine. The exposure to the three linear amines, however, led to similar changes in terms of intensity and speed of response, indicating no strong influence of the length of one-dimensional amines. This result is not surprising taking into account that linear amines may access into the structure of ZnTriad in a perpendicular manner (i.e. with the amine group aiming to the porphyrin), resulting in a similar accessibility in all cases irrespective of amine length. Therefore, it is possible to validate our hypothesis that the specific separation among tetrapyrroles in the tripodal porphyrin may lead to selective responses towards different sizes and shapes of the amines.
4. Conclusions

The comparison between tripodal ZnTriad and monomeric ZnTPP has shown that this multiporphyrin system can reduce the aggregation of porphyrins in films. ZnTPP deposition on glass resulted in completely unusable films after less than one hour due to extreme aggregation, while ZnTriad showed excellent stability.

ZnTriad films have shown good gas-sensing abilities upon their exposure to butylamine as testing gas, featuring intense and reversible spectral changes, fast response and repeatability after consecutive exposure-recovery cycles.

The exposure of ZnTriad films to aniline, tert-butyamine, hexylamine, butylamine and propilamine has resulted in selective responses towards the amines. The linear amines have produced the fastest and more intense spectral changes on ZnTriad films, followed by tert-butyamine and aniline.

Overall, the results indicate that ZnTriad is able to discriminate amines regarding their size and/or shape, and therefore it would be an excellent candidate for the inclusion in multisensor arrays.

Acknowledgments

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Optical detection of amine vapors using ZnTriad porphyrin thin films


DISCUSIÓN CONJUNTA

El objetivo general de esta tesis ha sido la preparación y estudio de películas de porfirinas por distintas técnicas para su evaluación como sensores ópticos de COVs y gases tóxicos. Los resultados obtenidos han sido descritos y discutidos de forma individual en los Capítulos 3-7. A continuación se expone una breve discusión conjunta de todos los resultados obtenidos en esta memoria.

Características de las películas sólidas de porfirinas

Se han utilizado tres metodologías diferentes para la creación de películas de porfirinas. Uno de los objetivos principales a la hora de crear estas películas ha sido evitar en lo posible los fenómenos de agregación, ya que se ha probado que estos empeoran las propiedades sensoras de las porfirinas. Al mismo tiempo, las capas deben poseer una elevada relación superficie/volumen para facilitar la entrada y salida de analitos, y su interacción con las moléculas de porfirina.

En primer lugar, se utilizó la técnica LB para obtener películas de EHO y EHO:C8A (Capítulo 3). Mediante espectroscopía UV-vis y microscopía AFM se comprobó que la presencia de C8A disminuye la agregación de las moléculas de EHO al mismo tiempo que hace la película más accesible a la entrada de moléculas gaseosas, gracias a la creación de una superficie irregular que aumenta la relación superficie/volumen, lo que es consistente con lo obtenido en otros estudios. Por otra parte, el análisis de las superficies por AFM reveló que el número de monocapas transferidas por LB determina la rugosidad superficial de las películas, aumentando esta hasta las 20 monocapas y permaneciendo prácticamente constante a partir de este punto, lo que permitió determinar el número idóneo de capas para su aplicación sensora.

Posteriormente, en los Capítulos 4, 5 y 6, se utilizaron películas microestructuradas de TiO₂ preparadas por GAPVD como soporte para las porfirinas. En este caso, las porfirinas elegidas contaron con grupos de ácido carboxílico mediante los que se realiza la unión al TiO₂, consiguiéndose un enlace químico que aporta estabilidad a la película. Estas películas mixtas de porfirina/TiO₂ demostraron ser ideales para la creación de dispositivos ópticos sensores. Por una parte, la estructura de TiO₂ presenta una elevada porosidad, por lo que su transparencia es elevada y permite realizar medidas ópticas de transmisión. Por otra parte, el anclaje químico entre porfirina y TiO₂ se realiza de forma sencilla y es muy estable, evitando en gran medida los procesos de agregación propios de las porfirinas.
Para profundizar en este tipo de películas, en los Capítulos 5 y 6 se estudió la influencia de la posición de los grupos de ácido carboxílico en el anclaje a la superficie de TiO$_2$ mediante el análisis de los espectros FT-IR y UV-vis de las porfirinas ancladas y sin anclar. Según los resultados obtenidos, las fenilporfirinas con cuatro grupos carboxílicos en la posición \textit{meta} de sus fenilos se enlanzan mediante estos cuatro grupos a la matriz de TiO$_2$, gracias a la orientación de estos de forma perpendicular al plano de la molécula. Con esta geometría de anclaje, las moléculas quedarían situadas de forma plana sobre la superficie de TiO$_2$, con lo que se evita que puedan moverse y agregarse, proporcionando una gran estabilidad a las películas. Por el contrario, las fenilporfirinas con uno o más grupos carboxílicos en la posición \textit{para} de sus fenilos se anclan por tan sólo por uno o dos de estos grupos a la matriz de TiO$_2$, con lo que las porfirinas quedarían orientadas de forma perpendicular a la superficie de TiO$_2$. Esta disposición permite a la porfirina un cierto rango de movimiento, lo que favorece la agregación entre las porfirinas cercanas y disminuye las capacidades sensoras de la película por el apilamiento de los macrociclos.

Por último, en el Capítulo 7 se utilizó una metodología alternativa para la creación de películas de porfirinas evitando su agregación. En este caso las películas se basaron en porfirinas tripodales de Zn, formadas por tres monómeros de porfirina unidos entre sí por un grupo triol. La influencia de la distribución tripodal en la agregación se estudió mediante la comparación de películas de ZnTriad con películas de ZnTPP, su unidad monomérica. Las películas se depositaron sobre vidrio por spin-coating, de forma que la interacción de las porfirinas con el soporte fue pequeña y las diferencias en los estados de agregación se debieron exclusivamente a las diferentes estructuras moleculares. La evolución temporal del espectro UV-vis de ambas porfirinas en la película mostró que ZnTriad forma películas estables en el tiempo y con una escasa agregación, mientras que ZnTPP se agrega rápidamente formando clusters de gran tamaño que hacen inviable su utilización como sensor óptico. Estas diferencias se basan en la distribución tripodal de ZnTriad, en la que sus tres subunidades quedan separadas entre sí, evitando la interacción entre sus macrociclos y por lo tanto la agregación intermolecular.

A pesar de las diferencias estructurales, las propiedades espectrales de la porfirina tripodal se mantuvieron muy similares a las de la porfirina simple, lo que indica que desde un punto de vista espectral sus tres macrociclos se comportan como si fueran independientes. Sin embargo, se ha informado de que el coeficiente de extinción molar correspondiente a cada una de las subunidades de la porfirina tripodal es aproximadamente el doble que en su correspondiente monómero, posiblemente debido a una disminución en su simetría, lo que puede ser beneficioso para la detección óptica de gases, debido a un aumento de la sensibilidad.
Propiedades sensoras de las películas de porfirinas

El objetivo final de la preparación de películas de porfirinas fue el análisis de sus propiedades sensoras frente a diferentes gases. Todos los casos presentados resultaron en una respuesta ópticamente detectable de las películas ante su exposición a los gases, aunque con diferencias que merecen ser descritas.

_Detección de NO₂_

La exposición de películas mixtas de porfirina/calixareno y porfirina/TiO₂ a NO₂, estudiada en los Capítulos 3 y 6, respectivamente, resultó en una importante modificación de sus espectros UV-vis. Esta modificación espectral es consistente con la descrita por otros autores para otras porfirinas y se ha explicado mediante un proceso de oxidación de las porfirinas por parte del NO₂, seguido de oxidación de las porfirinas por parte del NO₂. En el caso de las películas de porfirina/calixareno, se comprobó que la cinética de exposición a NO₂ depende de forma importante del grosor de la película que, a su vez, determina la rugosidad de la superficie. Este fenómeno está relacionado con la homogeneidad de la película. Una película irregular, con dominios a diferentes alturas, permite un mejor acceso de las moléculas gaseosas a las capas inferiores, mientras que películas más homogéneas limitan la difusión a través de ellas. De esta forma, las películas con menos capas, y por lo tanto menos grosor, tienden a ser más homogéneas. Al aumentar el número de capas, la superficie se vuelve más rugosa y más porosa, lo que se puede relacionar con la transferencia parcial de moléculas de la interfase aire-agua a los soportes de vidrio, revelada en estudios previos. Esto resulta en una mejora en la difusión de gases a su interior. Sin embargo esta tendencia se detiene al llegar a un determinado número de capas (20 en nuestro caso), ya que las últimas cubren a las anteriores permaneciendo la rugosidad prácticamente constante aunque se aumen te el grosor de la película. Por lo tanto, un número equilibrado de capas evita las desventajas de las películas compactas que limitan la difusión de gases, al mismo tiempo que se evita el efecto de enterramiento que se produce con un número elevado de capas.

Por otra parte, la exposición de los tres tipos de películas de porfirina/TiO₂ a NO₂ (Capítulo 6) reveló que las propiedades sensoras de las tres porfirinas carboxílicas son similares, no encontrándose diferencias sustanciales por las diferentes geometrías de anclaje al TiO₂. Sin embargo, la menor agregación y mayor estabilidad mostrada por las películas mixtas de m-TCPP/TiO₂ sugiere que estas son las mejores candidatas dentro de las porfirinas carboxílicas analizadas para ser utilizadas como sensor de NO₂.

_Detección de COVs_

En los Capítulos 4 y 5 se analizó el comportamiento de películas mixtas de
Discusión conjunta

porfirina/TiO$_2$ ante su exposición a varios COVs. Los cambios espectrales obtenidos mostraron en general respuestas rápidas, intensas, reversibles y reproducibles, demostrando que las películas preparadas son una buena elección para la detección de múltiples analitos. Esto es debido no sólo a las capacidades sensoras de las porfirinas utilizadas, sino a las características aportadas por los soportes de TiO$_2$. La alta porosidad de la microestructura columnar de los soportes permite una rápida difusión de las moléculas gaseosas hacia su interior, favoreciendo la interacción de estas con las moléculas de porfirina. Además, estos soportes permiten la formación de películas con una alta concentración de porfirinas, lo que facilita su monitorización óptica, pero reduciendo los fenómenos de agregación con respecto a otras técnicas. Esto ocurre gracias al anclaje químico existente entre TiO$_2$ y porfirina, que aporta estabilidad a las películas. Por otra parte, las películas obtenidas presentan una buena reproducibilidad, probablemente debido a la baja variabilidad en los soportes de TiO$_2$ y a una saturación completa de los sitios de anclaje durante la infiltración de porfirinas.

Para facilitar el análisis de los cambios espectrales producidos en las películas mixtas tras su exposición a los COVs se representó el espectro en diferencia correspondiente a cada caso en forma de imagen espectral. Estas imágenes se pueden interpretar como patrones de reconocimiento, y permiten distinguir de una forma sencilla los cambios en posición e intensidad de las bandas propias del espectro de las porfirinas. Todos los analitos estudiados en el Capítulo 4 presentan patrones de reconocimiento con características diferentes, lo que permite la identificación de cada uno de ellos. Esto sugiere que el grupo utilizado de películas mixtas de porfirina/TiO$_2$ posee unas características apropiadas para su inclusión en un array o conjunto de sensores, que implicaría la obtención de las imágenes de reconocimiento en tiempo real.

Aunque el sistema no se ha probado aún con mezclas de gases, la detección de gases de forma individual es posible, y una mayor selectividad puede conseguirse mediante la inclusión de más tipos de moléculas sensoras. Para este fin otros autores han utilizado, por ejemplo, indicadores ácido-base o colorantes solvatocrómicos$^{12}$, que actualmente se plantean como objeto de futuras investigaciones.

La misma metodología de representación mediante imágenes espectrales se utilizó en el Capítulo 5 para estudiar la influencia de la geometría de anclaje de las porfirinas a la superficie de TiO$_2$ en sus capacidades sensoras de COVs. Junto con el análisis de los espectros individuales y de la cinética de exposición, la información obtenida de estas imágenes muestra una clara influencia del anclaje sobre los cambios espectrales. De esta forma, las películas preparadas con porfirinas $m$-ZnTCPP ofrecen una respuesta más selectiva a los diferentes analitos utilizados que aquellas preparadas con $p$-ZnTCPP, al mismo tiempo que su intensidad y rapidez son mayores. Estas diferencias en el comportamiento sensor es una
consecuencia de la diferente posición de los grupos carboxílicos periféricos, cuyo anclaje a la matriz de TiO$_2$ causa diferentes estados de agregación en las películas. Por lo tanto, la utilización de derivados metálicos de $m$-TCPP en arrays de sensores múltiples es una estrategia válida para la creación y mejora de sistemas ópticos de detección de COVs.

**Discriminación de aminas por tamaños y forma**

En la detección de gases, la discriminación de compuestos dentro de una misma familia funcional continúa siendo un reto. Por este motivo, y a pesar de ser un grupo dentro de los COVs y de haberse incluido algunas de ellas en los analítos de estudio en los Capítulos 4 y 5, se realizó un análisis específico con diferentes tipos de aminas en el Capítulo 7 para evaluar las capacidades sensoras de la porfirina tripodal ZnTriad ante moléculas con este grupo funcional. La exposición de películas de ZnTriad a butilamina, utilizada como amina tipo, mostró cambios espectrales intensos, rápidos y reversibles, lo que indica que esta porfirina es apropiada para la detección de aminas. Para completar este estudio y comprobar la selectividad de la porfirina tripodal, se expusieron las películas de porfirina a cinco aminas primarias de tamaños crecientes y geometrías diferentes (lineal, plana y tridimensional). Al igual que en los Capítulos 4 y 5, se utilizó una representación en forma de imagen spectral para obtener patrones de reconocimiento que permitieran una mejor identificación de los cambios producidos en el espectro de las películas. En estos patrones de reconocimiento se observa que la exposición a cada una de las aminas produce un patrón de cambio diferente, lo que indica una buena selectividad por parte de las películas de ZnTriad. A través del cálculo de la fracción de cambio, junto con el análisis de la cinética de exposición y de los patrones de reconocimiento, se puede concluir que los cambios espectrales más intensos y rápidos se produjeron tras la exposición a las aminas lineales. Esto sugiere que la porfirina ZnTriad es capaz de discriminar distintos tipos de aminas en función de su tamaño y/o forma, por lo que sería un excelente candidato para su inclusión en arrays de sensores.

**Bibliografía**

CONCLUSIONES

Al final de cada uno de los capítulos que contienen los resultados obtenidos en esta memoria se incluye un conjunto de conclusiones específicas al estudio desarrollado en cada caso. Aquí se presentan las conclusiones generales obtenidas en esta tesis.

1. Las técnicas para reducir la agregación de porfirinas en soportes sólidos, como la utilización de calixarenos, el anclaje químico al soporte o la creación de porfirinas ramificadas, mejoran las capacidades sensoras de las películas creadas.
2. El grosor de las películas de EHO y calixareno preparadas por LB es determinante para la optimización de sus propiedades sensoras de NO₂.
3. Las películas microestructuradas de TiO₂ son apropiadas como soporte para porfirinas, gracias a su transparencia, porosidad y la posibilidad de un enlace químico.
4. El tipo de enlace entre porfirina carboxílica y TiO₂ determina el grado de agregación de las porfirinas y por lo tanto sus propiedades sensoras.
5. Las películas mixtas de porfirina y TiO₂ presentan en general unas excelentes capacidades para la detección de diversos COVs y NO₂, con respuestas intensas, rápidas y reproductibles.
6. La porfirina ZnTriad forma películas estables y poco agregadas por spin-coating gracias a su estructura tripodal, manteniendo las propiedades espectrales de su monómero.
7. Las películas de ZnTriad presentan una respuesta rápida, reversible y reproducible frente a su exposición a aminas, a la vez que permiten la discriminación de estas en función de su forma y/o tamaño.
8. La representación de los cambios producidos en el espectro de las porfirinas en forma de imagen espectral permite su utilización como patrones de reconocimiento.
CONCLUSIONS

Each of the chapters in this report ends with the specific conclusions relevant to the work described in it. The general conclusions obtained in this thesis are presented here.

1. The techniques designed to reduce aggregation of porphyrins on solid substrates, such as the utilization of calixarenes, the chemical anchoring to the substrate or the creation of branched porphyrins, improve the sensing capabilities of the prepared films.
2. The thickness of EHO and calixarene LB films is determining for the optimization of their NO\textsubscript{2} sensing properties.
3. Microstructured TiO\textsubscript{2} films are appropriate as substrates for porphyrins, owing to their transparency, porosity and the possibility of chemical binding.
4. The type of binding between carboxylic porphyrins and TiO\textsubscript{2} determines the aggregation state of porphyrins and, therefore, their sensing properties.
5. In general, composite porphyrin and TiO\textsubscript{2} films exhibit excellent capabilities for the detection of several VOCs and NO\textsubscript{2}, with intense, fast and reproducible responses.
6. ZnTriad films prepared by spin-coating are stable and barely aggregated, owing to the tripodal structure of the porphyrin, which at the same time maintains the spectral properties of its monomer.
7. ZnTriad films exhibit fast, reversible and reproducible responses upon their exposure to amines, allowing their discrimination according to size and/or shape.
8. The representation of the changes produced to the porphyrin spectrum as spectral images allows its utilization as recognition patterns.