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Y TERMODINÁMICA APLICADA
UNIVERSIDAD DE CÓRDOBA**

***ESTUDIO DE LA AGREGACIÓN DE COLORANTES
EN PELÍCULAS MIXTAS ULTRAFINAS***

Tesis Doctoral

Carlos María Rubia Payá

Córdoba, Julio 2015

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MIXTAS ULTRAFINAS*

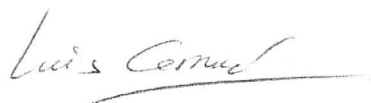
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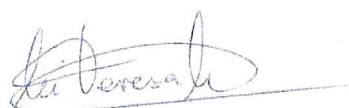
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**ESTUDIO DE LA AGREGACIÓN DE COLORANTES EN PELÍCULAS
MIXTAS ULTRAFINAS**

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Trabajo presentado para optar al grado de Doctor en Química



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INFORMA:

Que el trabajo presentado como Tesis Doctoral por D. Carlos M^a Rubia Payá, titulado "*Estudio de la Agregación de Colorantes en Películas Mixtas Ultrafinas*", ha sido realizado bajo mi dirección en los laboratorios de este Departamento y reúne las condiciones exigidas según la legislación vigente.

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TÍTULO DE LA TESIS: Estudio de la agregación de colorantes en películas mixtas ultrafinas

DOCTORANDO/A: Carlos M^a Rubia Payá

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(se hará mención a la evolución y desarrollo de la tesis, así como a trabajos y publicaciones derivados de la misma).

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El trabajo que engloba la presente Memoria se ha realizado durante el periodo de disfrute de contratos con cargo a proyecto financiado por la consejería de Economía, Innovación, Ciencia y Empleo de la Junta de Andalucía “*Películas Ultrafinas organizadas de colorantes orgánicos como componentes de dispositivos nanoestructurados*” (P10-FQM-6703) y también asociado a los proyectos financiados por la Consejería de Economía, Innovación, Ciencia y Empleo de la Junta de Andalucía “*Diseño de sistemas orgánicos nanoestructurados para su aplicación en dispositivos electroluminiscentes*” (P08-FQM-4011) y el Ministerio de Economía y Competitividad “*Desarrollo de nuevas estrategias para la formación de estructuras moleculares bi-dimensionales de películas delgadas. Incorporación en dispositivos nanoestructurados*” (CTQ2010-17481).

Objetivos	5
Capítulo I. Introducción	
Sección 1. Métodos de Preparación de Películas Delgadas	
1.1. Películas de Langmuir y Langmuir-Blodgett (LB)	11
1.2. Formación y Estudio de Monocapas en la Interfase Aire-Agua	12
1.3. Monocapas Mixtas de Lípido y Sustancias Solubles en Agua	15
1.4. Técnicas de Caracterización de Monocapas en la Interfase Aire-Agua	16
1.5. Películas de Langmuir-Blodgett	26
1.6. Técnicas de Caracterización de Películas Depositadas	30
Bibliografía	32
Sección 2. Métodos Espectroscópicos	
2.1. Fuerza y Polarización de Bandas de Absorción	35
2.2. Factor de Orientación en la Interfase Aire-Agua	37
2.3. Fuerza del Oscilador Aparente en la Interfase Aire-Agua	41
2.4. Interacción de la Radicación Electromagnética con Medios Absorbentes	42
2.5. Determinación de la Orientación Molecular sobre Soporte Sólido mediante Espectroscopía de Transmisión con Luz Polarizada	45
2.6. Determinación de la Orientación Molecular mediante Reflexión Con Luz Polarizada y Ángulo Variable en la interfase Aire-Agua	48
Bibliografía	55
Sección 3. Agregación	
3.1. Introducción	57
3.2. Modelo de los Dipolos Extendidos	58
3.3. Espectro UV-Visible de las Cianinas y sus Agregados	68
Bibliografía	72
Sección 4. Quiralidad	
4.1. Introducción y Conceptos	75
4.2. Quiralidad Supramolecular en un Plano	78
4.3. Importancia de la Quiralidad en Biología y en Química	80

4.4. Quiralidad en Interfases Modelo	82
Bibliografía	87
Capítulo II. Experimental	
Sección 1. Técnicas de Formación y Caracterización de Monocapas en la Interfase Aire-agua.	
1.1. Balanza de Langmuir	91
1.2. Espectroscopía de Reflexión Bajo Incidencia Normal	92
1.3. Espectroscopía de Reflexión Ultravioleta-Visible Bajo Incidencia Variable y Luz Polarizada	93
1.4. Microscopía de Ángulo Brewster (BAM)	94
1.5. Difracción y Reflectividad de Rayos X	96
1.6. Espectroscopía Infrarroja de Reflexión y Absorción con Modulación de la Polarización (PM-IRRAS)	97
Sección 2. Técnicas de Caracterización de Películas en la Interfase Aire-Sólido	
2.1. Transferencia de Monocapas a Sustratos Sólidos	99
2.2. Espectroscopia de Absorción UV-visible	100
2.3. Dicroísmo Circular (DC)	100
2.4. Espectroscopía de Fluorescencia.	101
Sección 3. Materiales, Reactivos y Tratamientos de Datos	102
Bibliografía	104
Resultados y Discusión	105
Capítulo III. Estudio de Monocapas de Acridina	
Sección 1. From 2D to 3D at the Air/Water Interface: The Self-Aggregation of the Acridine Dye in Mixed Monolayers	
1.1. Introduction	108
1.2. Experimental Section	111
1.3. Results and Discussion	113
1.4. Conclusion	131
References	133

Capítulo IV. Estudio de Monocapas de Cianina y Derivados

Sección 1. Chiral Structures in Quinoline Mixed Langmuir Monolayers

1.1. Introduction	140
1.2. Experimental Section	143
1.3. Results and Discussion	144
1.4. Conclusions	163
References	166
1.5. Supporting Information	172
References	178

Sección 2. Aggregation and Structural Study of the Monolayers

Formed by an Amphiphilic Thiapenta- Carbocyanine

2.1. Introduction	180
2.2. Results and Discussion	181
2.3. Conclusion	202
2.4. Experimental Section	206
References	208
2.5. Supporting Information	211
References	221

Conclusiones	223
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Resumen	227
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Otras aportaciones durante la tesis	237
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Anexo	291
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Objetivos

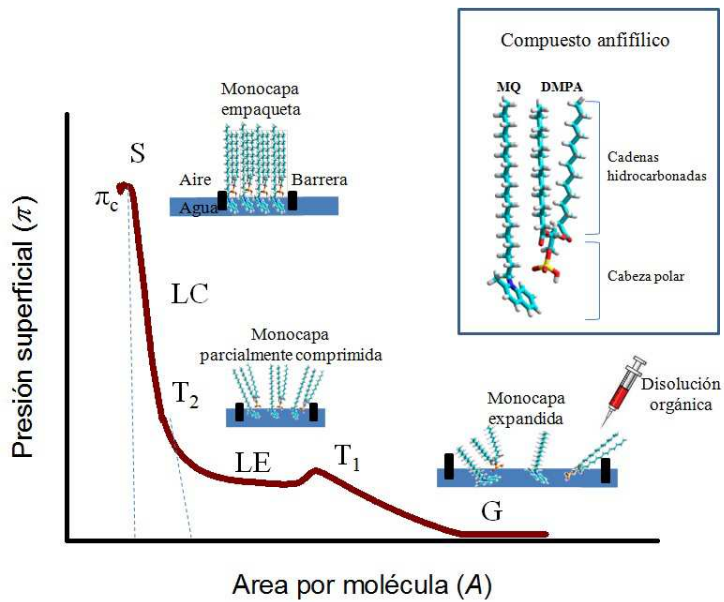


La presente Memoria presentada como Tesis Doctoral se encuadra en la línea de investigación “Películas Superficiales y Organización Molecular” del grupo FQM-204 de la Junta de Andalucía. Los objetivos globales que se han marcado son:

1. Preparar películas ultrafinas de materiales orgánicos de interés (lípidos y colorantes) en la interfase aire-agua. Estas películas mixtas estarán formadas por lípidos, tales como DMPA, SME, y colorantes anfífilos cargados como acridinas, cianinas y derivados de cianinas.
2. Realizar su posterior transferencia a soportes sólidos (vidrio, cuarzo e ITO) manteniendo su organización, mediante las técnicas de deposición vertical Langmuir-Blodgett, y horizontal, Langmuir-Schaefer, tanto en monocapa como en multicapa.
3. Estudiar, mediante diferentes técnicas de tipo óptico, la organización molecular de las películas formadas tanto en la interfase aire-agua como en la interfase aire-sólido.
4. Complementar y ampliar la descripción experimental de los sistemas estudiados mediante otro tipo de técnicas, tales como fluorescencia y sincrotrón.
5. Desarrollar modelos y métodos teóricos generales capaces de explicar la organización molecular de los sistemas objeto de estudio.

Capítulo I

Introducción



1. Métodos de Preparación de Películas Delgadas

1.1. Películas de Langmuir y Langmuir-Blodgett (LB)

Las primeras experiencias relacionadas con la formación de monocapas en la interfase aire-agua se remontan a los estudios llevados a cabo por Benjamin Franklin (1706-1790), cuando en 1773 se dio cuenta de que las olas de un estanque se calmaban al derramarse una cucharada de aceite sobre el agua, lo que Franklin no sabía, es que se había formado una monocapa de aceite sobre la superficie del agua. Más de un siglo después, Lord Rayleigh (1842-1919) cuantifica esta experiencia y confirma que el ácido oleico se había extendido uniformemente sobre la superficie del agua, y posteriormente calculó el espesor de la película obteniendo un valor de 1.6 nm.

Estos estudios estimularon a posteriores científicos a investigar de manera más profunda en este nuevo campo. Sin duda, la aportación más importante la realizó Irving Langmuir (1881-1957), que destacó por su trabajo en Química de Superficies, lo que le llevó a conseguir el Premio Nobel de Química en 1932. Su trabajo, junto con el de Lord Rayleigh, confirma que las capas de moléculas anfífilas esparcidas sobre superficies acuosas (películas de Langmuir) tienen el espesor de una capa molecular simple y concluyó que la orientación que presentan las moléculas en dicha superficie es con el grupo polar inmerso en el agua y la cadena alifática casi vertical a la superficie. Sus experimentos apoyaron la hipótesis de la existencia de interacciones de corto alcance y dieron la base sobre los distintos tipos de moléculas que pueden formar esta clase de películas.

Los avances más significativos de Langmuir se produjeron cuando colaboró junto a Katherine Blodgett (1898-1979), siendo la primera persona capaz de transferir monocapas de ácidos grasos desde la superficie del agua a soportes sólidos, en concreto vidrio hidrofílico, formando así las denominadas películas de Langmuir-Blodgett (LB).

Desde entonces hasta nuestros días, el abanico de posibilidades que ofrece esta técnica ha aumentado considerablemente. En la actualidad, la

técnica LB constituye una herramienta muy útil para la construcción de dispositivos supramoleculares, con una organización predefinida y con aplicaciones en diferentes áreas como óptica no lineal, sensores, electrónica molecular y fotocromismo.¹⁻⁶

1.2. Formación y Estudio de Monocapas en la Interfase Aire-Agua

Una molécula anfifílica posee una doble naturaleza, una parte apolar hidrofóbica constituida por una o varias cadenas alifáticas, y otra parte polar hidrofílica, con grupos funcionales tipo ácido, fosfato, alcohol o amina,⁷⁻⁸ como las que constituyen la monocapa del sistema 2-metil-1-octadecilquinoleína (MQ) : ácido 1,2-dimiristoil-*sn*-glicero-3-fosfato (DMPA) mostrada en la Figura 1.1.

La formación de monocapas en la interfase aire-agua se basa en la insolubilidad de las moléculas que las forman y, sobre todo, en la estructura anfifílica de las mismas.

La técnica de Langmuir, consiste en la preparación de monocapas sobre la superficie acuosa, mediante el esparcimiento o coesparcimiento de una cantidad determinada de moléculas anfifílicas, disueltas en un disolvente volátil e inmiscible en agua, las cuáles ocupan toda la superficie disponible (Figura 1.1). En este proceso, la elección del disolvente o mezcla de disolventes es importante, ya que debe favorecer la máxima dispersión de las moléculas sobre el agua.⁹

Una vez evaporado el disolvente, cabe esperar que la disposición de las moléculas en la interfase sea aquella en la que su situación energética resulte más favorable, esto es, con los grupos polares inmersos en la subfase acuosa y las colas hidrófobas fuera de la misma.⁷

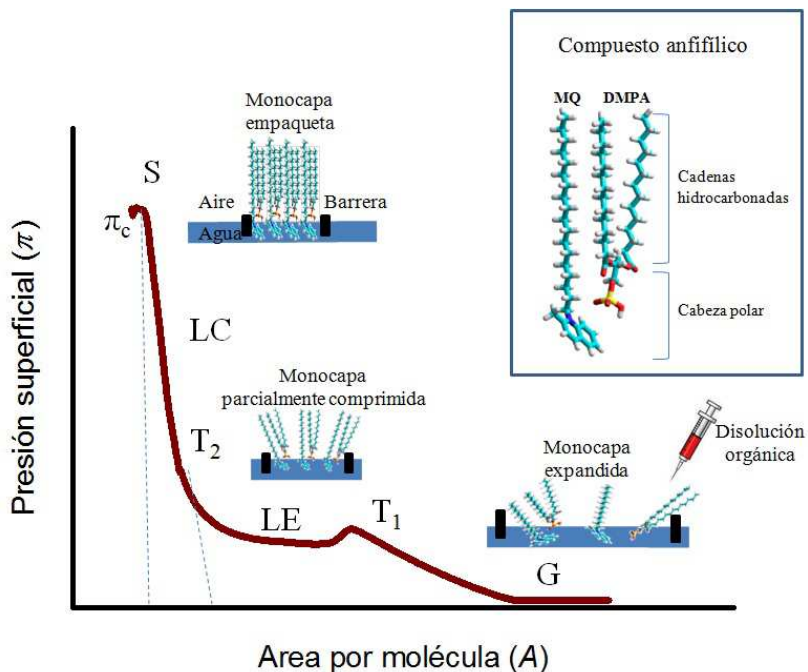


Figura 1.1. Isoterma π - A y esquema del proceso de compresión del sistema MQ:DMPA en la que se muestran las diferentes fases de la monocapa. En el cuadro interno se muestran las estructuras moleculares de MQ y DMPA.

De esta forma, la tensión superficial (γ) de la zona cubierta por la monocapa disminuye respecto a la tensión superficial de la superficie del agua limpia (γ_0) y como consecuencia, aparece una presión superficial (π) definida por:

$$\pi = \gamma_0 - \gamma \quad (1.1)$$

En principio, cualquier método para determinar la tensión superficial puede ser usado para medir la presión superficial. En la práctica se utilizan dos tipos de sistemas, el tipo Wilhelmy (sistema de detección mediante papel Wilhelmy y el tipo Langmuir (sistema de detección mediante flotador).¹⁰

Tras la evaporización del disolvente, la monocapa se comprime reduciéndose el área superficial disponible, de forma que la densidad superficial de las moléculas incrementa, disminuye γ y aumenta π . De esta

manera, la representación de π frente al área por molécula (A) aumenta cuando el área disminuye (ver Figura 1.1), siendo la analogía bidimensional de una isoterma presión-volumen.

Las isothermas π - A dan información de: la estabilidad de la monocapa en la interfase aire-agua, la organización de las moléculas en la monocapa y las interacciones entre ellas.

A partir de las isothermas π - A se obtienen dos parámetros muy importantes. Por una parte, el valor del área límite, obtenido por extrapolación del tramo de mayor pendiente de la isoterma a presión superficial cero, que se corresponde al área ocupada por una molécula en una situación de máximo empaquetamiento (líneas de puntos en la Figura 1.1). Y por otra, el valor máximo de presión superficial al cual la monocapa pierde su estabilidad, conocido con el nombre de presión de colapso (π_c en la Figura 1.1).

Las isothermas presión superficial-área muestran distintas regiones que corresponden a los diferentes estados de organización o fases en los que se encuentra la monocapa, así como regiones en las que coexisten dos fases.⁷ En la isoterma π - A mostrada en la Figura 1.1 se indican las fases para una película mixta MQ:DMPA = 1:1, descritas brevemente a continuación:

- Gaseosa (G): A muy bajas presiones superficiales, las moléculas se encuentran bastante diluidas en el seno de la monocapa y las interacciones entre ellas son débiles, constituyendo una fase denominada gas bidimensional.
- Líquida: Cuando la presión superficial aumenta se llega a una fase fluida muy compresible, en la que las moléculas experimentan unas fuerzas atractivas lo suficientemente intensas como para que empiecen a adoptar una estructura compacta, formándose lo que se llama líquido expandido (LE). Entre estas dos fases descritas ocurre un proceso parecido a la condensación de un gas, es decir, una zona de coexistencia de ambos estados, G + LE (T1). Aumentos posteriores de presión dan lugar a un estado menos compresible y más ordenado, conocido como líquido condensado (LC). La organización de la monocapa es compacta y la parte hidrófoba de las moléculas se orienta

perpendicularmente a la interfase. De nuevo, puede observarse una segunda transición de fase entre la situación de líquido expandido y la de líquido condensado, LE + LC (T2).

- Sólido (S): Al continuar comprimiendo la monocapa, y antes de que ésta llegue al colapso, se alcanza un estado sólido (S) donde la película es muy rígida y las cadenas hidrófobas forman un apilamiento compacto.

No obstante, hay que indicar que el número y la complejidad de las fases observadas en una isoterma varían en función del sistema estudiado y de las condiciones experimentales bajo las cuales se realizan las isotermas.

1.3. Monocapas Mixtas de un Anfílico y Sustancias Solubles en Agua.

El método tradicional para la formación de películas de Langmuir requiere el empleo de moléculas anfílicas. De esta forma, la gama de moléculas que podían formar monocapas estables era limitada. En las últimas décadas del siglo XX, se han desarrollado métodos que permiten utilizar una gran variedad de moléculas para la formación de este tipo de películas, incluso moléculas solubles en agua. Estos métodos están basados en la construcción de monocapas complejas, donde los componentes de la monocapa se organizan bajo control externo y atendiendo a las interacciones intermoleculares específicas de cada sistema. Uno de los métodos propuestos consiste en añadir sustancias solubles en la subfase acuosa, de forma que la sustancia pueda adsorberse sobre una matriz lipídica/anfílica seleccionada y así permanecer en la interfase. Más efectivo, sin embargo, se ha mostrado el método denominado de coespargimiento, en el cual la sustancia se coespargue en la misma disolución mezclada con el anfílico sobre la superficie acuosa,¹¹⁻¹⁴ de tal forma que el adsorbato queda retenido en la interfase mediante interacciones, principalmente electrostáticas. Sobre esta base, se ha ampliado el rango de moléculas que pueden ser estudiadas mediante la técnica de Langmuir en la interfase aire-agua.

1.4. Técnicas de Caracterización de Monocapas en la Interfase Aire-Agua.

Además de las medidas de presión superficial-área, en la balanza de Langmuir, existe una gran variedad de técnicas, en continua evolución, muy útiles en la caracterización de películas superficiales en la interfase aire-agua. En la Tabla 1.1 se recogen algunas de las técnicas más importantes usadas en la caracterización de las monocapas en la interfase aire-agua, así como los parámetros medidos y la información obtenida a partir de ellas.

Tabla 1.1. Técnicas de caracterización de monocapas en la interfase aire-agua.

<i>Técnicas</i>	<i>Parámetro medido</i>	<i>Información</i>
Presión Superficial	π versus A	Área por molécula Presión de colapso Fases de la monocapa
Potencial Superficial	ΔV versus A	Dipolos superficiales Orientación de los grupos polares
Reflexión con incidencia normal	ΔR	Densidad molecular Orientación y agregación del colorante
Reflexión con incidencia variable	ΔR	Índice de refracción y espesor de la monocapa Orientación de las diferentes componentes de absorción
Viscosidad superficial	η_s	Cambios de viscosidad
Elipsometría	Polarización de La luz reflejada	Índice de refracción y espesor de la monocapa
Difracción de rayos X (GIXD) y (XRR)	Reflectividad	Espaciado y estructura en capas empaquetadas
Generación de segundos armónicos	Polarización de la susceptibilidad del segundo armónico	Valor medio del ángulo entre el eje de la molécula y la normal a la interfase
Espectroscopia IR con transformada de Fourier	Reflectividad	Orientación media de las cadenas alifáticas de las moléculas en la monocapa
Microscopia de fluorescencia	Fluorescencia de una molécula sonda	Estructura de la monocapa y evolución de las fases
Microscopía de ángulo Brewster (BAM)	Reflectividad	Morfología de la monocapa y comportamiento de las fases

A continuación se describen con más detalle aquellas técnicas que han sido utilizadas en el trabajo presentado en esta Memoria.

Espectroscopía de Reflexión UV-Vis, de incidencia normal a la interfase aire-agua

Esta técnica se basa en la diferencia de reflectividad de una superficie acuosa cubierta con una monocapa y una superficie acuosa limpia (ver Figura 1.2). Utiliza luz no polarizada, la cual se hace incidir de forma normal sobre la superficie del agua.

Denominaremos R_S y $R_{D,S}$ a las cantidades de radiación reflejadas en ausencia y en presencia de monocapa, respectivamente. Cuando la reflexión y la absorción son pequeñas, se cumple aproximadamente que:¹⁵

$$R_{D,S} = R_S + R_D + A\sqrt{R_S} \quad (1.2)$$

donde R_D y A son la reflexión y la absorción propias de la monocapa, respectivamente.

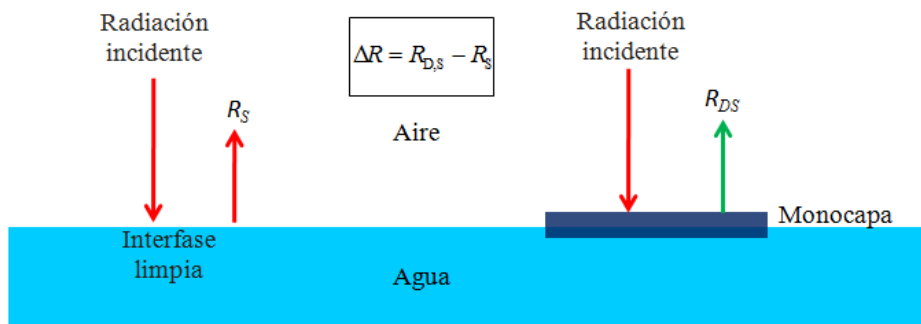


Figura 1.2. Esquema de la Espectroscopía de Reflexión en la interfase aire-agua.

El término $A\sqrt{R_S}$ representa la amplificación de la luz reflejada a consecuencia de la absorción. Asimismo, $R_D \approx A \times A_M/4$, donde A_M es la absorción máxima.

$R_{D,S}$ y R_S se determinan simultáneamente en una misma experiencia, por lo que la medida experimental es directamente la diferencia entre ambas

$$\Delta R = R_{D,S} - R_S = A \left(\sqrt{R_S} + \frac{A_M}{4} \right) \approx A \sqrt{R_S} \quad (1.3)$$

En general, la absorción de la monocapa es lo suficientemente pequeña como para despreciar el término $A_M/4$. Asimismo, en este caso, absorción y absorbancia están relacionadas mediante el factor numérico 2.303, por lo que:

$$\Delta R = 2.303 \times 10^3 f_o \varepsilon \sqrt{R_S} \Gamma \quad (1.4)$$

donde ε representa la absorptividad molar en sus unidades habituales ($\text{mol}^{-1}\text{L}^{-1}\text{cm}$), Γ es la concentración superficial en molcm^{-2} , $R_S = 0.02$, f_o es el factor de orientación y el factor numérico 10^3 da cuenta del cambio de unidades necesario para que ΔR sea adimensional. El factor de orientación f_o compara las orientaciones promedio del dipolo de transición en disolución y en la interfase aire-agua y su introducción es necesaria ya que, la absorptividad molar se define como la que posee el cromóforo en disolución.

La ecuación anterior nos propone un método para detectar la presencia de cromóforos en la interfase aire-agua a partir de medidas del incremento de la reflexión de la monocapa con respecto a la interfase limpia, permitiendo cuantificar el material existente en dicha interfase y obtener, como se describirá más adelante, información sobre la orientación del cromóforo.

Espectroscopía de Reflexión UV-visible bajo ángulo variable y luz polarizada (RAV) en la interfase aire-agua

La espectroscopía de reflexión de ángulo variable fue desarrollada por el grupo del Prof. Dietmar Mobius a mediados de la década de los 80.¹⁵⁻¹⁷ Esta técnica proporciona información sobre la inclinación y agregación de los cromóforos en películas de Langmuir. Igual que la Espectroscopía de Reflexión de incidencia normal, se basa en la diferencia de reflectividad de una superficie acuosa cubierta con una monocapa y una superficie acuosa

limpia, si bien utiliza luz polarizada, que incide a diferentes ángulos (Figura 1.3).

Mediante la técnica de Reflexión de ángulo variable, al incidir radiación p-polarizada a ángulos de incidencia mayores al ángulo de Brewster es posible resolver bandas con diferente polarización, ya que la banda de absorción se descompone en una parte positiva y otra negativa en función de la polarización de sus componentes.

A partir de las ecuaciones de Fresnel para luz polarizada s y p, y en función del ángulo de incidencia α_0 , se pueden determinar los coeficientes de reflexión para materiales biaxiales anisótropos en sustratos isotrópicos como aire o el agua.¹⁸ Mediante un método de ajuste es posible calcular el parámetro de orden $P(\theta)$ de cada componente de la banda de absorción, así como los parámetros ópticos como: índice de refracción n_1 , espesor de la película d , valor de la constante de absorción k_{iso} (ver sección 2 de este Capítulo).

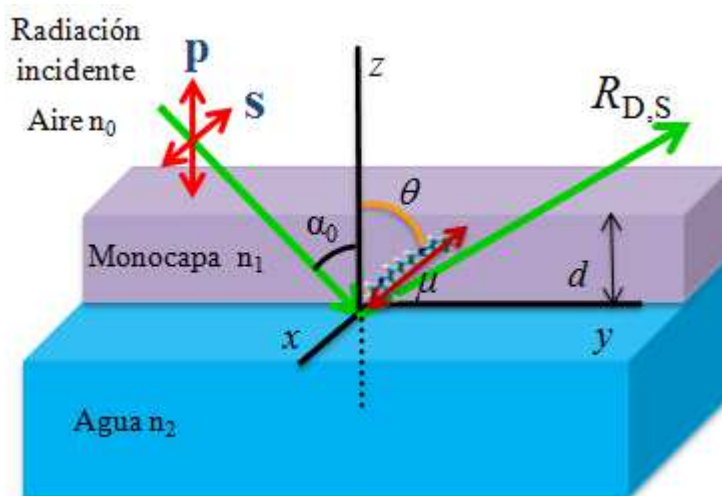


Figura 1.3. Esquema de Espectroscopia de Reflexión de ángulo variable y luz polarizada en la interfase aire-agua. La flecha verde representan la luz incidente y la flecha granate representa la dirección del dipolo de transición de la molécula, μ .

Microscopía de ángulo Brewster (BAM)

La microscopía de ángulo Brewster es una herramienta excelente para el estudio de monocapas, ya que sólo registra la reflectividad debida a las moléculas situadas en la interfase aire-agua.^{19,20} Esta técnica fue desarrollada en 1991 por S. Henon²¹ y D. Honig,²² como un método directo y no invasivo para el estudio de la morfología y el estudio de las películas de Langmuir.

La reflectividad en la interfase de dos medios se define como la relación entre la fracción de intensidad reflejada e intensidad incidente.²³ Esta relación depende de la polarización de la radiación y del ángulo de incidencia. El fenómeno de polarización por reflexión se produce cuando un haz de luz no polarizada incide desde un medio con índice de refracción n_1 , a otro medio de mayor índice de refracción n_2 , con un ángulo i tal que el rayo refractado forma un ángulo recto con el reflejado. Además, la polarización producida por este fenómeno es siempre perpendicular al plano de incidencia (polarización s). Aplicando la condición anterior a la ley de Snell ($n_1 \text{sen}i = n_2 \text{sen}r$), se obtiene la ley de Brewster ($\text{tg}i = n_2/n_1$, $n_2 > n_1$), esquematizada en la Figura 1.4.

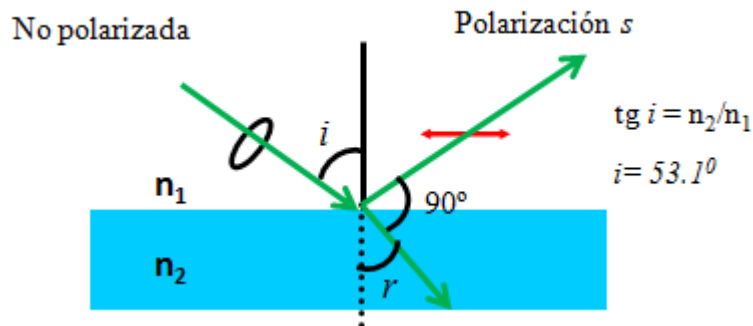


Figura 1.4. Esquema de polarización por reflexión.

La microscopía de ángulo Brewster se basa en este principio. Cuando se hace incidir un haz de luz en la interfase aire-agua con polarización paralela al plano de incidencia (polarización p) y bajo el ángulo Brewster

$i = 53.1^\circ$ para esta interfase, toda la radiación es transmitida, no produciéndose reflexión alguna. Si ahora se esparce una monocapa de moléculas sobre la subfase acuosa se forma una nueva interfase, donde los índices de refracción son n_{aire} y n_{monocapa} , y en la que el ángulo Brewster disminuye ligeramente. En estas condiciones, y si mantenemos el ángulo de incidencia original, parte de la luz se refleja, debido únicamente a la presencia de la monocapa. Si, a continuación, esta radiación es recogida por una cámara, podemos observar directamente la morfología de la película durante su proceso de formación (Figura 1.5). Además, su posterior análisis puede aportar valiosa información acerca de la organización molecular dentro de la película. Así, por ejemplo, teniendo en cuenta que la polarizabilidad de una cadena hidrocarbonada extendida es mayor a lo largo del eje que perpendicular al mismo, la anisotropía óptica de los dominios puede ser observada mediante BAM.

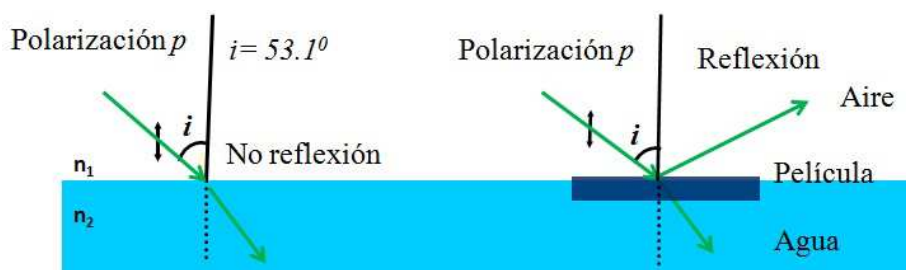


Figura 1.5. Principio físico de la microscopía de ángulo de Brewster, BAM.

Esta técnica, frente a otras como la microscopía de fluorescencia, ofrece mayor contraste en aquellos dominios con diferente orientación azimutal,²⁴ además de no necesitar una sonda fluorescente que añadir a la película, lo que puede influir en la organización y morfología de la película.

Difracción de rayos X de incidencia rasante (GIXD)

La difracción de rayos X de incidencia rasante es una técnica de caracterización microestructural de películas en la interfase aire-agua que usa una fuente de rayos X de alta intensidad, que inciden en la película de forma casi paralela a dicha interfase. Esta técnica fue introducida por Kjaer, Dutta y

col,²⁵⁻²⁷ y se ha establecido como una poderosa herramienta para estudiar el empaquetamiento de moléculas anfifílicas en la interfase aire-agua (Figura 1.6).

Los rayos X de alta intensidad se generan por la colisión de positrones en un acelerador de partículas tipo sincrotrón, y son convertidos en un rayo monocromático ($\lambda=1.3038\text{\AA}$) gracias a un cristal monocromador de Be. Este rayo se hace incidir sobre la monocapa a un ángulo de incidencia de $\alpha_i=0.85\alpha_c$, siendo $\alpha_c\approx 0.13^\circ$ el ángulo crítico para la reflexión total. Sólo los primeros 80 Å por debajo de la superficie del agua son iluminados, para mejorar la sensibilidad de las monocapas y eliminar ruido de fondo. Con un detector sensible a la posición lineal se recoge la luz difractada en función del ángulo de dispersión vertical α_f . El ángulo de dispersión en el plano (horizontal) 2Θ se varía rotando todo el dispositivo detector. Siendo \vec{k}_i , el vector en la dirección de la radiación incidente y \vec{k}_f el vector en la dirección de la radiación dispersada.

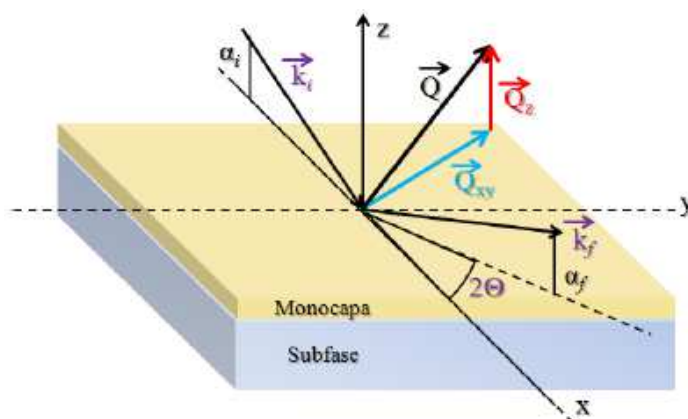


Figura 1.6. Esquema de la Técnica GIXD en la interfase aire-agua.

Las componentes horizontal (Q_{xy}) y vertical (Q_z) del vector de dispersión se pueden expresar de la siguiente forma:

$$Q_{xy} \approx \frac{4\pi}{\lambda} \text{sen} \frac{2\Theta}{2} \quad (1.5)$$

$$Q_z \approx \frac{2\pi}{\lambda} \text{sen}(a_f) \quad (1.6)$$

donde λ es la longitud de onda de los rayos X. La intensidad de la radiación detectada se corrige en función de la polarización, el área efectiva y el factor de Lorentz. Los picos obtenidos en la dirección del plano se ajustan por mínimos cuadrados a una curva Lorentziana y los picos fuera del plano a una Gaussiana. La semianchura (anchura a mitad del máximo, AMM) de los picos obtenidos en la dirección del plano está relacionada con la longitud de correlación l , es decir, la extensión de la red cristalina, en la forma:²⁸ $l=2/AMM$. Los picos obtenidos en la dirección fuera del plano son llamados “barras de Bragg”, y su anchura es inversamente proporcional a la longitud de la molécula. Por la posición de los picos en la dirección del plano (horizontal), se puede determinar el espaciamiento de red:

$$d(hk) = \frac{2\pi}{Q_{xy}^{hk}} \quad (1.7)$$

donde (h, k) indica el orden de reflexión. Los parámetros de red a , b y el ángulo γ se pueden estimar desde el espaciamiento de red $d(hk)$, pudiendo calcular el área por celda unidad A_{xy} :

$$A_{xy} = a \cdot b \cdot \text{sen}(\gamma) \quad (1.8)$$

Las moléculas anfífilas sólo se pueden empaquetar en un número limitado de redes cristalinas: hexagonal, ortorrómbica y oblicua. En una red hexagonal, las cadenas están normalmente perpendiculares a la interfase, con unos parámetros de red $a=b$ y $\gamma=120^\circ$. Cuando las cadenas están totalmente inclinadas de forma simétrica es una fase ortorrómbica, y sólo dos picos de Bragg son detectados. Cuando la inclinación es intermedia tenemos una fase oblicua, y se pueden ver tres picos de difracción.

Reflectividad especular de rayos X (XRR)

Las medidas de reflectividad especular de rayos X se realizan en el mismo instrumento que las de difracción GIXD. Para las medidas de reflectividad, los ángulos del rayo incidente α_i y reflejado α_f son iguales, y se varían en el rango $0.5 \alpha_c < \alpha_i (\alpha_f) < 30 \alpha_c$, donde $\alpha_c = 0.13^\circ$. La luz reflejada es medida con un detector de centelleo de NaI en el plano del rayo incidente, en función del vector de dispersión fuera del plano Q_z .

En el caso de una interfase ideal y bien definida entre gas y líquido, la reflectividad ($R_f(Q)$) es simplemente una reflectividad tipo Fresnel. Una monocapa de grosor d modula la reflectividad en vectores de onda del orden de π/d y superiores. La reflectividad medida (R), dividida por la reflectividad de Fresnel viene dada por la fórmula:²⁹

$$\frac{R}{R_f} = \frac{1}{\rho_w^2} \left| \rho'(z) \cdot e^{iQ_z z} dz \right|^2 \quad (1.9)$$

donde ρ_w es la densidad electrónica del agua, ρ' el gradiente de densidad electrónica a lo largo del vector normal Q_z . En realidad la interfase entre dos fases no está matemáticamente bien definida. La rugosidad molecular, σ , es del orden de los 3 Å y está causada principalmente por excitaciones térmicas en la superficie del agua. Es por ello que hay que introducir el factor Debye-Waller ($e^{-Q_z^2 \sigma^2}$) en la fórmula.

Adicionalmente, no se puede aplicar directamente una transformada de Fourier a la reflectividad para obtener la distribución de densidad electrónica, porque se mide el cuadrado absoluto de un número complejo y no la fase. Por este motivo, la reflectividad medida tiene que ser ajustada a un perfil de densidad con un número de parámetros ajustable: el modelo de cajas.

En una versión simplificada del modelo de cajas, la monocapa de Langmuir es considerada como dos cajas que representan la región de las cadenas alifáticas y el grupo polar, con densidades electrónicas constantes. Este modelo tiene 4 parámetros ajustables: altura (densidad) y anchura (longitud de los segmentos) de las dos cajas, y un parámetro general que

representa la rugosidad. Este modelo es capaz de describir satisfactoriamente la región de las colas alifáticas, aunque no es tan bueno para la determinación de la orientación y la hidratación del grupo polar.

Espectroscopia infrarroja de absorción-reflexión con modulación de polarización (PM-IRRAS)

La técnica de PM-IRRAS permite determinar la orientación molecular de los grupos funcionales y de toda la molécula o de todo un sistema molecular, como por ejemplo, en las monocapas de Langmuir mediante la comparación de las intensidades máximas, o mediante el cálculo de un espectro teórico.³⁰⁻³¹

Las relaciones de los máximos relativos de los grupos funcionales se pueden utilizar para determinar la inclinación de las moléculas con respecto a la interfase. En la técnica de PM-IRRAS, la luz infrarroja se resuelve en las componentes, s (paralela a la interfase) y p (perpendicular a la interfase), utilizando un modulador fotoelástico (PEM)³²⁻³⁴ a una frecuencia alta (Figura 1.7). En esta técnica se define la diferencia de reflectividad como:

$$\Delta R = R_p - R_s \quad (1.10)$$

Dividiendo la diferencia de reflectividades entre la suma de reflectividades.³⁵⁻³⁷

$$S \approx \Delta R / S = (R_p - R_s) / (R_p + R_s) \quad (1.11)$$

siendo $R = R_p + R_s$, se obtiene la relación de reflectividades o señal S, en la cual se compensa la reflectividad de la subfase. Sólo la absorción anisotrópica contribuye a la señal, S, del PM-IRRAS, como es el caso de monocapas de lípido y colorante. Se pueden obtener directamente las señales normalizadas a través de la expresión:

$$\Delta S = (S_d - S_0) / S_0 \quad (1.12)$$

donde S_d y S_0 son las señales obtenidas en presencia y en ausencia de monocapa. Por este tratamiento matemático, se pueden detectar las reflectividades de las diferentes especies moleculares en las interfases sólido-gas,³⁸⁻⁴⁰ gas-

líquido⁴¹⁻⁴² y sólido-líquido.⁴³⁻⁴⁶ En comparación con la técnica IRRAS, la modulación de alta frecuencia permite detectar las polarizaciones de la luz reflejada, (R_s) y (R_p), de forma cuasi-simultánea.

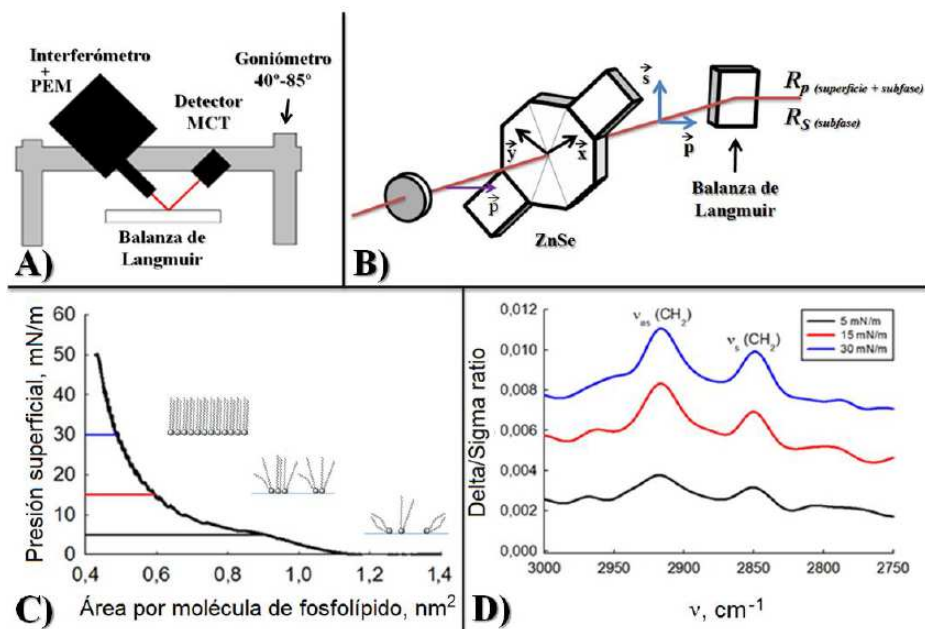


Figura 1.7. Esquema de un experimento de PM-IRRAS. A) Esquema del instrumento. B) Esquema fundamento físico del PEM.⁴⁷ C) Isotherma π -A del fosfolípido (DPPC), donde se muestran las presiones superficiales a las cuales se registraron los interferogramas. D) Interferogramas a distintas presiones superficiales.

1.5. Películas de Langmuir–Blodgett

Existe un gran interés hacia la construcción de sistemas formados por moléculas que interactúan entre sí, son los denominados ensamblajes moleculares organizados. Una forma sencilla de construir estos sistemas es mediante la incorporación de moléculas activas en monocapas de matrices lipídicas apropiadas, y ensamblarlas en monocapas de una manera predeterminada. Cada monocapa es producida en la interfase aire-agua mediante esparcimiento de las moléculas de una forma adecuada, para posteriormente ser fijada sobre un soporte sólido formando estructuras supramoleculares con características definidas.

Con el objeto de construir, ensamblar y manipular películas simples, preparadas previamente en la interfase aire-agua, Langmuir y Blodgett desarrollaron la denominada técnica de Langmuir-Blodgett (LB),⁴⁸⁻⁴⁹. Sin embargo, la posibilidad de construir sistemas organizados complejos mediante el ensamblaje de monocapas, de forma controlada, a través de dicha técnica, fue impulsada a principios de los 60 debido, en gran parte, al trabajo realizado por Kuhn y col⁵⁰. En particular el estudio enfocado en la transferencia de energía entre monocapas, ha dado nombre a las películas Langmuir-Blodgett-Kuhn (LBK).

La técnica LB consiste en colocar un soporte sólido perpendicular a la interfase aire-agua cubierta por la monocapa que se va a transferir, y mediante inmersión y/o emersión, de dicho soporte, las moléculas se van depositando sobre el sustrato sólido (Figura 1.8). Durante la transferencia se hace avanzar la barrera móvil para compensar la pérdida de moléculas y mantener constante la presión superficial (mecanismo feed-back).

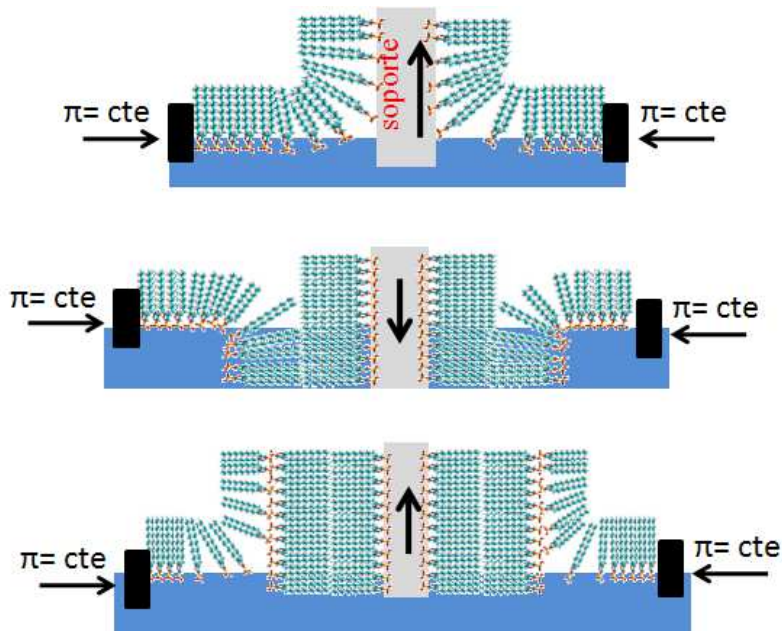


Figura 1.8. Esquema de la transferencia de monocapas de un fosfolípido desde la interfase aire-agua a un soporte sólido mediante el método de Langmuir-Blodgett (LB).

Asimismo, Langmuir y Schaefer⁵¹ describieron una técnica de deposición horizontal o “touching” (Figura 1.9), en la que un soporte se sitúa de forma paralela a la superficie cubierta por la monocapa. Así, la transferencia de la monocapa se efectúa con el levantamiento del soporte de la interfase.

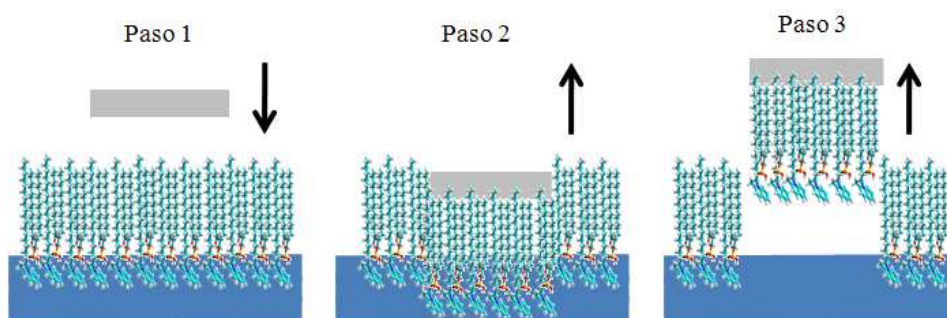


Figura 1.9. Esquema de la transferencia de una película mixta desde la interfase aire-agua a un soporte sólido según el método de Langmuir-Schaefer (LS).

En la bibliografía se pueden encontrar otros métodos de transferencia⁷ en los que la interacción existente entre la subfase, monocapa y sustrato sólido cambia con respecto a los anteriores. Así, se encuentra el método de contacto de Schulman⁵² y el de Kossi y Leblanc,⁵³ quienes han publicado una técnica que combina la deposición vertical con la de contacto para la fabricación de sistemas modelo de membrana.

El método de Langmuir-Blodgett (LB) es una técnica clásica en Química de Superficies, actualmente no se conocen todos los mecanismos por los que las monocapas en la interfase aire-agua se transfieren a los sustratos sólidos.¹⁻² Sobre esta base, las interacciones moleculares implicadas en la deposición de la primera capa pueden ser bastante diferentes de las responsables de la transferencia de las siguientes. Para algunos materiales, la deposición de la película parece estar asociada con un cambio de fase, desde una fase bidimensional líquido cristalino sobre la interfase acuosa a una forma sólida cristalina fuertemente empaquetada sobre el sustrato. Sin embargo, después de muchas evidencias experimentales y tratamientos teóricos, no

siempre pueden explicarse fenómenos como los diferentes modos de transferencia y/o la velocidad óptima a la que los diferentes materiales pueden depositarse.

La fabricación de películas LB requiere de una gran destreza para conseguir una buena deposición de las monocapas, así como una buena calidad de las mismas, controlando cuidadosamente todas las variables experimentales relacionadas con ésta para alcanzar los mejores resultados. Estas variables pueden ser: estabilidad y homogeneidad de las moléculas que forman la monocapa; composición, fuerza iónica, pH, temperatura de la subfase; naturaleza del sustrato (estructura y carácter hidrofóbico o hidrofílico); velocidad de inmersión y emersión del soporte; ángulo de penetración del sustrato en la subfase; presión de compresión durante el proceso de deposición; o número de monocapas transferidas.

En la Figura 1.8 se muestra un ejemplo de la transferencia de una monocapa sobre un soporte sólido mediante la técnica LB. En este caso, el sustrato es hidrofílico y la primera monocapa se transfiere cuando el sustrato es sacado de la subfase, por lo que dicho sustrato tendría que estar localizado dentro de la subfase antes de esparcir la monocapa. En este modo de deposición denominado tipo Y (Figura 1.10, izquierda), el ordenamiento de la película es centro-simétrico, estableciéndose una configuración cabeza-cabeza y cola-cola en las sucesivas transferencias.⁵⁴ En la bibliografía¹⁻² se encuentran películas tipo X, en la cual la deposición de la monocapa se efectúa únicamente en la inmersión del soporte a través de la interfase, y la deposición de tipo Z, en la que la monocapa se transfiere solamente al emerger el sustrato de la subfase, en ambos casos las películas que se consiguen son centro-asimétricas (Figura 1.10, centro y derecha). Es de destacar que el ordenamiento molecular final en una monocapa LB, no siempre es tan perfecto como aparece en la Figura 1.10, ya que en muchos caso se produce una reorganización de las moléculas en las películas depositadas durante el proceso de transferencia.

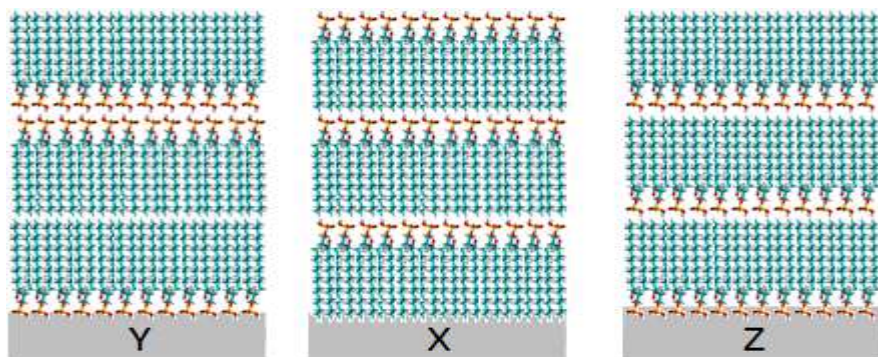


Figura 1.10. Tipos de deposición.

Con objeto de cuantificar el grado de transferencia desde la interfase aire-agua a la interfase aire-sólido, se usa la denominada relación de transferencia, τ , dada por Langmuir y colaboradores:

$$\tau = \frac{A_L}{A_S} \quad (1.13)$$

donde A_L es la disminución del área ocupada por la monocapa sobre la interfase aire-agua, a presión constante, y A_S es el área cubierta del sustrato sólido. Valores de τ , próximos a la unidad indican una transferencia prácticamente completa de la monocapa de una superficie a otra.

1.6. Técnicas de Caracterización de Películas Depositadas

Una vez formada la película LB, para estudiar su arquitectura y organización, es necesario conocer los diferentes factores que afectan a la estructura supramolecular de la misma. Con este objeto se pueden utilizar diversas técnicas espectroscópicas de caracterización como: Espectroscopia de adsorción UV-Vis, usando luz polarizada y no polarizada y bajo diferentes ángulos de incidencia; Espectroscopia IR con transformada de Fourier y Raman (SERS); Dicroísmo circular (DC); Elipsometría; Difracción de Rayos X; Microscopias de ángulo Brewster (BAM), electrónica de barrido (SEM) y de transmisión (TEM), de efecto túnel (STM) o de fuerza atómica (AFM).

Estas técnicas constituyen un grupo de herramientas muy importante dentro de este campo, puesto que mediante ellas no sólo se obtiene información sobre la densidad de las moléculas soportadas sino también de los detalles acerca de la estructura (orden), morfología (topografía) y composición, permitiendo determinar el tamaño, orientación e interacción entre los dominios formados, así como datos de los defectos de la película. Toda esta información ayuda a construir los modelos de organización de las moléculas en la película.

Tabla 1.2. Técnicas de caracterización de películas depositadas.

<i>Técnicas</i>	<i>Parámetro medido</i>	<i>Información</i>
Microscopía electrónica de barrido (SEM)	Dispersión de electrones y Rayos X	Composición, estructura y topografía en monocapas empaquetadas Composición y distribución de elementos
Microscopía electrónica de transmisión. (TEM)	Dispersión y Difracción de electrones	Morfología, estructura y composición de monocapas empaquetadas Determinación de la red cristalina y composición del cristal
Microscopía electrónica de fuerza atómica (AFM)	Fuerza atómica	Topografía de una película a escala atómica
Microscopía electrónica de efecto túnel (STM)	Diferencia de voltaje	Visualización de una película a escala atómica
Elipsometría	Polarización de la luz reflejada	Índice de refracción y espesor de la monocapa
Dicroísmo circular (DC)	Diferencia de absorbancia de luz polarizada	Quiralidad de una monocapa
Difracción de rayos X (GIXD) y (XRR)	Reflectividad	Espaciado y estructura en capas empaquetadas
Espectroscopia IR con transformada de Fourier y RAMAN (SERS)	Reflectividad	Orientación media de las cadenas alifáticas de las moléculas en la monocapa
Microscopía de fluorescencia	Fluorescencia de una molécula sonda	Estructura de la monocapa
Microscopía de ángulo Brewster (BAM)	Reflectividad	Morfología de la monocapa

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2. Métodos Espectroscópicos

2.1. Fuerza y Polarización de Bandas de Absorción

La intensidad de una banda de absorción electrónica suele representarse en términos de la denominada *fuerza del oscilador*, f .¹ Esta puede calcularse a partir de la integración de la banda:

$$f = \frac{4\varepsilon_0 2.303 m_e c_0}{N_A e^2} \int_{\text{banda}} \varepsilon d\nu = 1.44 \times 10^{-19} \int_{\text{banda}} \varepsilon d\nu \quad (2.1)$$

donde ε es la absorptividad molar, ε_0 la permitividad en el vacío, m_e y e la masa y carga del electrón, c_0 la velocidad de la luz en el vacío, y N_A el número de Avogadro. En la ecuación anterior, el factor numérico $1.44 \cdot 10^{-19}$ tiene unidades de $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm} \cdot \text{s}$. La fuerza del oscilador, f , es una magnitud adimensional que relaciona la absorción total de una transición espectroscópica (integral de la banda) con la absorción del oscilador clásico equivalente.

Transiciones permitidas por las reglas de selección espectroscópicas dan lugar a valores de f del orden de la unidad. Se obtienen valores de $f \ll 1$ cuando la transición considerada incumple alguna de las reglas de selección.

A partir de la ecuación de Schrödinger dependiente del tiempo, es posible obtener una relación teórica para la fuerza del oscilador:

$$f = \frac{8 \cdot \pi^2 m_e n g}{3 h^2 e^2 \hat{n}} M^2 \Delta E = 2.128 \times 10^{-75} \frac{n g M^2 \Delta E}{\hat{n}} \quad (2.2)$$

donde h es la constante de Planck, \hat{n} , el índice de refracción, g la degeneración del estado excitado, n el número de electrones en el estado ocupado (HOMO), E la energía de la transición espectroscópica, y M es el módulo del vector momento dipolar de transición. En esta ecuación, el factor numérico $2.128 \cdot 10^{-75}$ tiene unidades de $\text{C}^{-2} \text{m}^{-2} \text{J}^{-1}$. La deducción de la ecuación (2.2) implica suponer que el vector momento dipolar de transición se encuentra en la dirección del campo eléctrico de la luz incidente.

El vector dipolo de transición se define como:

$$\vec{M} = e \int \psi_i \vec{r} \psi_j d\tau = M_x \vec{i} + M_y \vec{j} + M_z \vec{k} \quad (2.3)$$

donde ψ_i y ψ_j son las funciones de onda de los estados inicial y final de la transición. Para moléculas lineales, con estados excitados no degenerados, solo una de las componentes del vector dipolo de transición es diferente de cero. Esto sucede por ejemplo con el grupo acridina (DAO), estudiada en esta Tesis.

Sin embargo, en moléculas planas con centro de simetría, como en el caso de las porfirinas, existe degeneración y el dipolo de transición posee dos componentes diferentes de cero, de forma que, la dirección de este (en realidad su cuadrado) se encuentra uniformemente distribuida en un círculo contenido en el plano de la molécula.

La absorción de radiación depende de la orientación relativa entre la radiación incidente y el dipolo de transición. Únicamente la componente \vec{M} que oscila en la misma dirección que el campo eléctrico de la radiación, da lugar a absorción molecular. Matemáticamente esto puede expresarse mediante la relación,

$$|\vec{\mathcal{E}} \cdot \vec{M}|^2 = (M_x^2 + M_y^2 + M_z^2) |\vec{\mathcal{E}} \cdot \vec{n}|^2 = M^2 |\vec{\mathcal{E}} \cdot \vec{n}|^2 \quad (2.4)$$

donde $\vec{\mathcal{E}}$ y \vec{n} son los vectores característicos de la radiación incidente y de la dirección del dipolo, respectivamente. En la ecuación (2.2) se ha supuesto que el producto $|\vec{\mathcal{E}} \cdot \vec{n}|^2 = 1$, por lo que, en un caso general, la ecuación (2.2) debe ser modificada para tener en cuenta este efecto, multiplicándola por el factor $|\vec{\mathcal{E}} \cdot \vec{n}|^2$.

La absorción de radiación tiene lugar cuando el producto escalar $|\vec{\mathcal{E}} \cdot \vec{n}|^2 \neq 0$, es decir, si dichos vectores son perpendiculares no se produce absorción. A consecuencia de este fenómeno, los sistemas moleculares organizados, tales como cristales moleculares y películas

superficiales, son ópticamente activos y pueden polarizar la luz incidente. Este fenómeno puede utilizarse para determinar la orientación molecular en sistemas organizados.

2.2. Factor de Orientación en la Interfase Aire-Agua

Supongamos una molécula lineal, con una sola componente diferente de cero en su dipolo de transición (por ejemplo, la acridina). En disolución, donde la orientación es al azar, la absorción debe ser proporcional a un factor $2/3$. En efecto, podemos imaginar que $1/3$ de las moléculas se encuentran alineadas hacia cada uno de los ejes de coordenadas, por lo que, si la radiación incidente lo hace a lo largo de un eje determinado, solo dos de las orientaciones anteriores darán lugar a absorción de radiación. Sin embargo, si las moléculas se encuentran en la interfase aire-agua con su dipolo de transición orientado paralelo a la interfase, la absorción debe de ser proporcional a un factor 1, ya que en esta situación la molécula siempre es capaz de absorber radiación (ver Figura 2.1). El factor de orientación se define como el cociente entre estas dos cantidades, $1/(2/3) = 3/2$, lo que nos indica que, a igualdad de densidad molecular, la absorción puede llegar a ser 1.5 veces superior a la absorción en disolución.

Una definición general del factor de orientación debe realizarse en base a la ecuación (2.4). Si definimos los ejes de coordenadas tal como se hace en la Figura 2.1, y suponemos que la radiación incide a lo largo del eje z, independientemente de que el experimento se realice en disolución o en la interfase aire-agua, los vectores $\vec{\epsilon}$ y \vec{n} tendrán la forma:

$$\vec{\epsilon} = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad \vec{n} = \begin{pmatrix} \text{sen}(\theta)\cos(\omega) \\ \text{sen}(\theta)\text{sen}(\omega) \\ \cos(\theta) \end{pmatrix} \quad (2.5)$$

donde θ es el ángulo que forma el dipolo de transición de la molécula con respecto al eje z (normal a la interfase aire-agua), y ω el ángulo que forma la proyección del dipolo de transición en el plano x-y, con el eje x, según se

observa en la Figura 2.1.

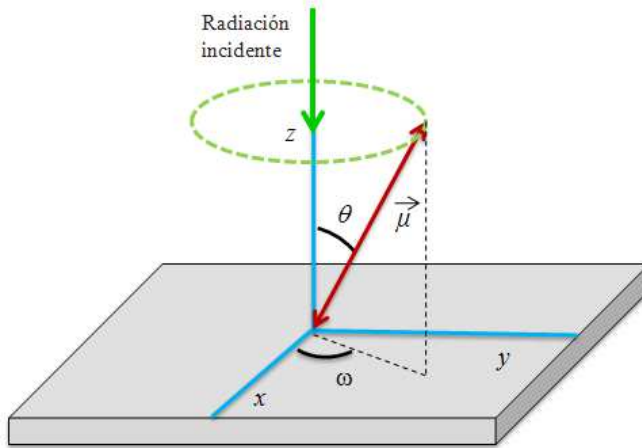


Figura 2.1. La flecha roja indica la dirección del vector dipolo de transición μ , y la flecha verde indica la radiación incidente.

Asimismo, e independientemente del medio en el que se realice el experimento tendremos que:

$$M^2 |\vec{\mathcal{E}} \cdot \vec{n}|^2 = M^2 \left(\langle \text{sen}(\theta)^2 \cos(\omega)^2 \rangle + \langle \text{sen}(\theta)^2 \text{sen}(\omega)^2 \rangle \right) \quad (2.6)$$

donde el símbolo $\langle \rangle$ indica valores promedio. Si el medio es isotrópico en el plano x-y (plano de la interfase), no existirá dirección preferente de orientación con respecto al ángulo ω (ver Figura 2.1), por lo que puede escribirse que,

$$\langle \text{sen}(\theta)^2 \cos(\omega)^2 \rangle + \langle \text{sen}(\theta)^2 \text{sen}(\omega)^2 \rangle = \frac{\langle \text{sen}(\theta)^2 \rangle}{2} + \frac{\langle \text{sen}(\theta)^2 \rangle}{2} = \langle \text{sen}(\theta)^2 \rangle \quad (2.7)$$

Supondremos que esta condición se cumple en la interfase aire-agua y, como es lógico, en disolución. El factor de orientación, por lo tanto, puede definirse, cuando existe isotropía en el plano x-y de la interfase, como

$$f_0 = \frac{|\vec{\mathcal{E}} \cdot \vec{n}|_{\text{aire-agua}}^2}{|\vec{\mathcal{E}} \cdot \vec{n}|_{\text{disolución}}^2} = \frac{\langle \text{sen}(\theta)^2 \rangle_{\text{aire-agua}}}{\langle \text{sen}(\theta)^2 \rangle_{\text{disolución}}} \quad (2.8)$$

El valor medio de $\text{sen}(\theta)^2$, viene definido por

$$\langle \text{sen}(\theta)^2 \rangle = \frac{\int_0^\pi \text{sen}(\theta)^2 F(\theta) \text{sen}(\theta) d\theta}{\int_0^\pi F(\theta) \text{sen}(\theta) d\theta} \quad (2.9)$$

donde $F(\theta)$ representa la función de distribución de los dipolos con respecto al ángulo θ (ver Figura 2.1). En disolución, debe existir también isotropía con respecto al eje z , por lo que $F(\theta)$ es constante e igual a:

$$\langle \text{sen}(\theta)^2 \rangle_{\text{disolución}} = \frac{F(\theta) \int_0^\pi \text{sen}(\theta)^2 \text{sen}(\theta) d\theta}{F(\theta) \int_0^\pi \text{sen}(\theta) d\theta} = \frac{2}{3} \quad (2.10)$$

De esta forma, el factor de orientación f_0 viene dado por:²

$$f_0 = \frac{3}{2} \langle \text{sen}(\theta)^2 \rangle_{\text{aire-agua}} = \frac{3}{2} \text{sen}(\theta)^2 = \frac{3}{2} P(\theta) \quad (2.11)$$

donde se define el parámetro de orden $P(\theta)$, como al valor promedio de $\langle \text{sen}(\theta)^2 \rangle$.

Si la orientación es homogénea, es decir, si todos los dipolos tienen el mismo ángulo θ de inclinación, $F(\theta)$ será una función discontinua, tal que solo es diferente de cero para dicho ángulo, en este caso $\langle \text{sen}(\theta)^2 \rangle = \text{sen}(\theta)^2$, cumpliéndose la relación de la ecuación (2.11). En caso contrario, es decir, cuando la distribución de los dipolos no es homogénea, esta sustitución no puede ser realizada. En la interfase aire-agua, las películas superficiales homogéneas de cromóforos muestran, en general, una orientación preferente.

Dicha orientación, además, puede ser alterada modificando la presión superficial. En estos casos, la determinación del factor de orientación permite obtener información cuantitativa del grado de inclinación de los dipolos, como se pone de manifiesto en los Capítulos III y IV de esta Memoria.

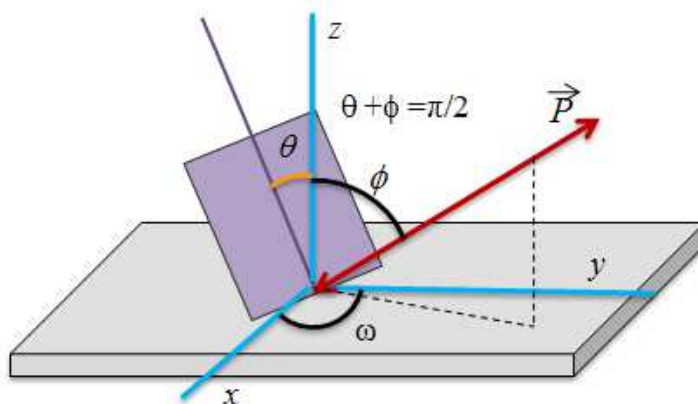


Figura 2.2 La flecha roja representa el vector \vec{P} , perpendicular al plano de la molécula.

Para moléculas con dos componentes de su dipolo de transición diferentes de cero, planas (p. ej. porfirinas), puede seguirse el mismo procedimiento al descrito con anterioridad, si bien, en este caso, el tratamiento debe de ser aplicado a las dos componentes del dipolo. Supondremos el plano de la molécula orientado un ángulo θ con respecto al eje z , tal como se muestra en la Figura 2.2. Se define el vector \vec{P} , como el vector dirección perpendicular al plano de la molécula, siendo ϕ el ángulo entre el eje z y este vector, por lo que $\theta + \phi = \pi/2$. Para cada eje, la suma de las componentes al cuadrado de los dipolos, debe ser igual a uno menos la componente del vector \vec{P} al cuadrado, por lo que, en este caso

$$M^2 |\vec{\epsilon} \cdot \vec{n}|^2 = M^2 (|\vec{\epsilon} \cdot \vec{u}|^2 - |\vec{\epsilon} \cdot \vec{p}|^2) \quad (2.12)$$

siendo

$$\vec{u} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad \vec{p} = \begin{pmatrix} \text{sen}(\phi) \cos(\omega) \\ \text{sen}(\phi) \text{sen}(\omega) \\ \cos(\phi) \end{pmatrix} \quad (2.13)$$

Suponiendo isotropía en el plano x-y, y que, por lo tanto, la ecuación (2.7) es aplicable, y que en disolución la ecuación (2.11) se cumple para el ángulo ϕ , puede escribirse que

$$f_0 = \frac{|\vec{\epsilon} \cdot \vec{n}|_{\text{aire-agua}}^2}{|\vec{\epsilon} \cdot \vec{n}|_{\text{disolución}}^2} = \frac{2 - \langle \text{sen}(\phi)^2 \rangle_{\text{air-ag}}}{2 - \langle \text{sen}(\phi)^2 \rangle_{\text{dis}}} = \frac{3}{4} \left(1 + \langle \cos(\phi)^2 \rangle_{\text{air-ag}} \right) = \frac{3}{4} \left(1 + \langle \text{sen}(\theta)^2 \rangle \right) \quad (2.14)$$

Al igual que en el caso anterior $\langle \text{sen}(\theta)^2 \rangle = \text{sen}(\theta)^2$ solo cuando existe una distribución homogénea de todos los dipolos.

2.3. Fuerza del Oscilador Aparente en la Interfase Aire-Agua

Con frecuencia la reflexión suele expresarse de una forma normalizada. Si se tiene en cuenta que

$$\Gamma = \frac{10^{14}}{N_A S} \quad (2.15)$$

donde S corresponde al área ocupada por molécula en la interfase, expresada en nm^2 , es posible escribir la expresión (1.4), dada en la Sección 1 de esta Introducción, como

$$\Delta R = 2.303 \times 10^3 f_0 \epsilon \sqrt{R_S} \Gamma = \frac{2.303 \times 10^{17} f_0 \epsilon}{N_A S} \sqrt{R_S} \quad (2.16)$$

lo que nos permite definir la reflexión normalizada como

$$\Delta R_{\text{norm}} = S \times \Delta R = \frac{2.303 \times 10^{17} f_0 \epsilon}{N_A} \sqrt{R_S} = 5.545 \times 10^{-8} f_0 \epsilon \quad (2.17)$$

donde se ha utilizado $\sqrt{R_s} = 0.145$, y ΔR_{norm} posee unidades de $\text{nm}^2/\text{molécula}$.

La combinación de las ecuaciones (2.1) y (2.17) nos propone un procedimiento para el cálculo de la fuerza del oscilador a través de la integración de la banda de reflexión normalizada:

$$f = \frac{1.44 \times 10^{-19}}{5.545 \times 10^{-8} f_0} \int_{\text{banda}} \Delta R_{\text{norm}} d\nu = \frac{2.6 \times 10^{-12}}{f_0} \int_{\text{banda}} \Delta R_{\text{norm}} d\nu \quad (2.18)$$

Sin embargo, el factor de orientación es una magnitud desconocida a priori, por lo que conviene definir una fuerza del oscilador aparente mediante la relación:

$$f_{\text{ap}} = f \times f_0 = \frac{3}{2} f \times P(\theta) = 2.66 \times 10^{-12} \int_{\text{banda}} \Delta R_{\text{n}}^N d\nu \quad (2.19)$$

donde el factor $2.6 \cdot 10^{-12}$ tiene unidades de $\text{nm}^{-2} \text{ s}$. Hay que indicar que, en la anterior definición f es la fuerza del oscilador en disolución (condiciones isotrópicas).

Las variaciones de ΔR_{norm} o f_{ap} con la presión superficial en la interfase aire-agua y en particular, la disminución de dichos valores pueden ser relacionadas con dos fenómenos: bien con una pérdida de cromóforo hacia la subfase acuosa, o bien con una reorientación del dipolo de transición. Por lo tanto, cuando la pérdida de cromóforo puede ser descartada, las variaciones de ΔR_{norm} o f_{ap} con el área superficial permiten determinar la orientación del dipolo de transición.

2.4. Interacción de la Radiación Electromagnética con Medios Absorbentes

La interacción entre una onda electromagnética y un material anisotrópico que absorbe radiación, puede describirse mediante los llamados parámetros ópticos, relacionados con la función dieléctrica del material.

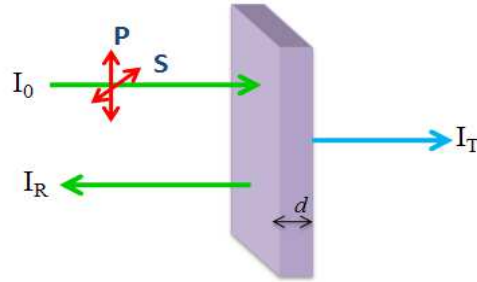


Figura 2.3. La flecha verde indica la radiación incidente y reflejada, y la flecha azul la radiación transmitida a través de la película.

Si llamamos I_0 a la radiación incidente, I_R a la radiación reflejada e I_T a la radiación transmitida, como se muestra en la Figura 2.3, se define la reflectividad del material, R como:

$$R = \frac{I_R}{I_0} \quad (2.20)$$

De igual forma si llamamos, α al coeficiente de absorción del material y d al espesor, la radiación transmitida viene dada por la siguiente expresión:

$$I_T = I_0(1 - R)e^{-\alpha d} \quad (2.21)$$

Estos parámetros están relacionados con la constante dieléctrica del material ϵ , que es una magnitud compleja y se define por la siguiente expresión:

$$\epsilon = \epsilon' + i\epsilon'' \quad (2.22)$$

donde ϵ' y ϵ'' son las constantes dieléctrica y de absorción de dicha película.

Para materiales anisotrópicos con índice de refracción complejos:

$$N = n - ik, \quad (2.23)$$

siendo n la parte real del índice de refracción y k la constante de absorción.

La relación entre el índice de refracción complejo de la película N , y la constante dieléctrica viene dada por la relación $\varepsilon = N^2$. Combinando ambas expresiones (2.22 y 2.23), se obtiene:

$$\begin{aligned} \varepsilon' + i\varepsilon'' &= (n - ik)^2 = n^2 - k^2 + i2nk; \\ \varepsilon' &= n^2 - k^2 \quad \text{y} \quad \varepsilon'' = 2nk \end{aligned} \quad (2.24)$$

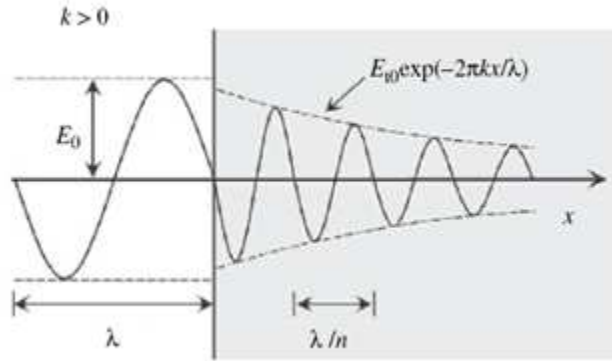


Figura 2.4. Radiación electromagnética que se transmite a través de un medio absorbente.

El valor de la constante de absorción k , puede expresarse en función del coeficiente de absorción α , según la relación a incidencia normal (ver Figura 2.3):

$$k = \frac{\lambda}{4\pi} \alpha = \frac{2.303}{4\pi} \cdot \frac{\lambda \cdot Abs}{d} \quad (2.25)$$

El coeficiente de absorción α , y la absorbancia Abs , se relacionan según la ecuación (1.4) mediante el factor numérico 2.303. Así la intensidad de una radiación que atraviesa un medio absorbente como se muestra en la Figura 2.4, puede expresarse en función de la absorbancia de la siguiente manera:

$$I = I_0 e^{-\alpha d} = I_0 10^{-Abs} \quad (2.26)$$

2.5. Determinación de la Orientación Molecular sobre Soporte Sólido mediante Espectroscopía de Transmisión con Luz Polarizada

El empleo de luz linealmente polarizada permite determinar directamente la orientación molecular en películas superficiales. Uno de los métodos utilizado para ello consiste en hacer incidir radiación polarizada, s y p, sobre el soporte, con un ángulo de inclinación α_0 (ver Figura 2.5), determinándose experimentalmente la relación dicróica $\Delta T_s/\Delta T_p$. Esta relación es función de α_0 , así como de la orientación del dipolo de transición, θ .

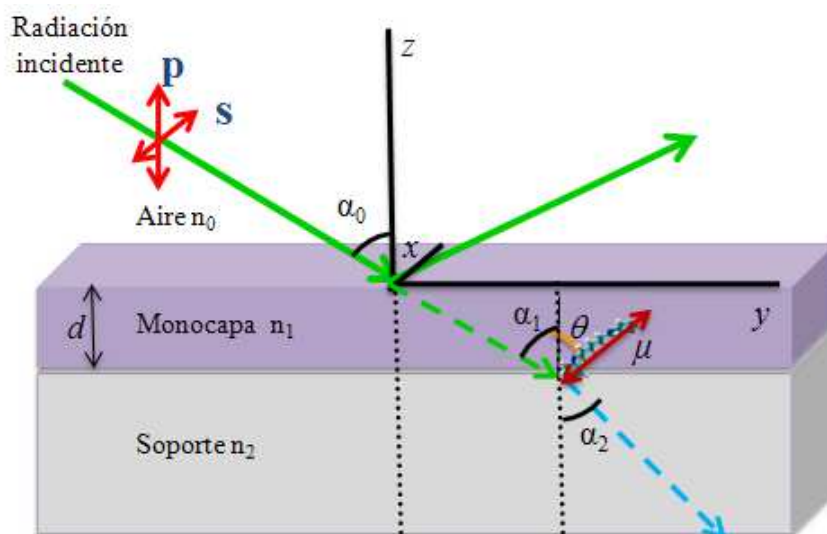


Figura 2.5. La flecha verde indica la radiación incidente polarizada con un ángulo de inclinación α_0 , la flecha azul la radiación refractada con un ángulo de inclinación α_2 , la flecha granate la orientación del dipolo de transición de las moléculas de la película, μ .

Los modelos teóricos que permiten predecir la relación $\Delta T_s/\Delta T_p$ son complejos y pueden clasificarse en modelos macroscópicos (Vandevyver y col.³ y de Yoneyama y col.⁴), en los que a la película superficial se le asignan propiedades dieléctricas como a cualquier material macroscópico, y en modelos microscópicos (Möbius y col.⁵), donde la película superficial es analizada como un cristal bidimensional de dipolos puntuales.⁵

En el Modelo de Vandevyver y col.³ las propiedades ópticas de la

película superficial son descritas en base al tensor dieléctrico complejo, ecuación (2.22) $\mathcal{E} = \mathcal{E}' + i\mathcal{E}''$ y para cada eje. Las componentes de la diagonal de este tensor, serán las magnitudes de interés de cara a la absorción. La absorción en s y p vienen dadas por las relaciones:³

$$A_s = \frac{4\eta}{2.3} \frac{\mathcal{E}_{yy}''}{n_0 \cos(\alpha_0) + n_2 \cos(\alpha_2)} \quad (2.27)$$

$$A_p = \frac{4\eta}{2.3} \frac{n_0 n_2}{n_0 \cos(\alpha_2) + n_2 \cos(\alpha_0)} \left[\frac{n_0^2 \text{sen}(\alpha_0)^2 \mathcal{E}_{zz}''}{\mathcal{E}_{zz}'^2 + \mathcal{E}_{zz}''^2} + \frac{\cos(\alpha_0) \cos(\alpha_2)}{n_0 n_2} \mathcal{E}_{xx}'' \right] \quad (2.28)$$

donde n_0 y n_2 son los índices de refracción del aire y el soporte respectivamente, α_2 es el ángulo de refracción en el substrato (ver Figura 2.5), el cual puede determinarse a partir de la ley de Snell [$n_0 \text{sen}(\alpha_0) = n_2 \text{sen}(\alpha_2)$] y $\eta = 2\pi d/\lambda$, siendo d el espesor de la película, y λ la longitud de onda de la radiación. En estas expresiones, se ignora la posible reflexión interna múltiple y, se supone que la absorción es pequeña.

En el trabajo original en el que este modelo fue desarrollado,³ se propone como método de análisis la función denominada *dicroísmo lineal*, definida como $LD = A_s - A_p$. Sin embargo, el parámetro utilizado en esta memoria es la relación dicroica $\Delta T_s/\Delta T_p$, por lo que se describirá brevemente como puede ser deducida.

Identificando las absorciones de las ecuaciones (2.27) y (2.28) directamente con la transmisión, puede escribirse que:

$$\frac{\Delta T_s}{\Delta T_p} \approx \frac{A_s}{A_p} = \frac{n_0 \cos(\alpha_2) + n_2 \cos(\alpha_0)}{n_0 \cos(\alpha_0) + n_2 \cos(\alpha_2)} \left[\frac{n_0^3 n_2 \text{sen}(\alpha_0)^2}{\mathcal{E}_{zz}'^2 + \mathcal{E}_{zz}''^2} \frac{\mathcal{E}_{zz}''}{\mathcal{E}_{yy}''} + \cos(\alpha_0) \cos(\alpha_2) \frac{\mathcal{E}_{xx}''}{\mathcal{E}_{yy}''} \right]^{-1} \quad (2.29)$$

Las expresiones para las diferentes componentes de \mathcal{E}'' dependen de la degeneración y de la orientación del dipolo de transición. Dicha orientación puede ser especificada mediante el mismo procedimiento que el utilizado para definir el factor de orientación. Así, cuando solo una de las componentes del

dipolo es diferente de cero, la dirección del dipolo viene fijada por las ecuaciones (2.4) y (2.5), de forma que se cumple:³

$$\varepsilon''_{xx} = A_0 \langle \cos(\omega)^2 \text{sen}(\theta)^2 \rangle = \frac{A_0}{2} \langle \text{sen}(\theta)^2 \rangle \quad (2.30)$$

$$\varepsilon''_{yy} = A_0 \langle \text{sen}(\omega)^2 \text{sen}(\theta)^2 \rangle = \frac{A_0}{2} \langle \text{sen}(\theta)^2 \rangle \quad (2.31)$$

$$\varepsilon''_{zz} = A_0 \langle \cos(\theta)^2 \rangle \quad (2.32)$$

donde A_0 es una constante y los términos de la derecha de las ecuaciones anteriores son válidos para orientaciones isotrópicas en el plano x-y (ver Figura 2.1). Para determinar la relación $\Delta T_s/\Delta T_p$, falta conocer el término ε''_{zz} . Para estos sistemas no degenerados, que en general se componen de moléculas con una cadena alifática larga y un grupo cromóforo pequeño, puede escribirse de forma aproximada que $\varepsilon''_{zz} + \varepsilon''_{zz} \approx \varepsilon''_{zz} = n_1^4$, donde n_1 es el índice de refracción de la película. Este, en general, es desconocido, pero si la cadena alifática es lo suficientemente larga puede utilizarse el de dicha cadena, siendo $n_1 \approx 1.43$,³ o valores típicos de monocapas de Langmuir que van desde $1.75 \geq n_1 \geq 1.45$. Teniendo en cuenta lo indicado anteriormente, puede escribirse para sistemas no degenerados que

$$\frac{\Delta T_s}{\Delta T_p} \approx \frac{n_0 \cos(\alpha_2) + n_2 \cos(\alpha_0)}{n_0 \cos(\alpha_0) + n_2 \cos(\alpha_2)} \left[\frac{n_0^3 n_2 \text{sen}(\alpha_0)^2 2 \langle \cos(\theta)^2 \rangle}{n_1^4 \langle \text{sen}(\theta)^2 \rangle} + \cos(\alpha_0) \cos(\alpha_2) \right]^{-1} \quad (2.33)$$

Al igual que en apartados anteriores, los valores promedio pueden ser sustituidos por $\text{sen}(\theta)^2$ o $\cos(\theta)^2$, solo cuando la distribución de dipolos sea homogénea. En la Figura 2.6 se muestra la representación de $\Delta T_s/\Delta T_p$ vs θ según la ecuación (2.33), suponiendo distribución homogénea, para $\alpha_0 = 45^\circ$ y $\alpha_0 = 65^\circ$, utilizando $n_1 = 1.6$ y $n_2 = 1.52$.

Para $\theta = 90^\circ$, se obtiene que $\Delta T_s/\Delta T_p = 1.56$, si bien este valor depende de α_0 . Así, por ejemplo, para $\alpha_0 = 65^\circ$ y $\theta = 90^\circ$ se obtiene que $\Delta T_s/\Delta T_p = 2.75$.

Para $\theta = 0^\circ$, $\Delta T_s/\Delta T_p = 0$, independientemente de α_θ . Asimismo, a partir de la expresión anterior (ecuación 2.33) se puede determinar si existe o no anisotropía en el plano x-y (ver Figura 2.1). De esta forma, si la distribución es isotrópica en el plano, debe cumplirse que $\Delta T_s/\Delta T_p = 1$ para $\alpha_\theta = 0$, en caso contrario $\Delta T_s/\Delta T_p \neq 1$. Por último, cuando la distribución de dipolos en la película es al azar, $\langle \text{sen}(\theta)^2 \rangle = \langle \text{cos}(\theta)^2 \rangle$, se obtiene que $\Delta T_s/\Delta T_p = 1.189$ para $\alpha_\theta = 45^\circ$.

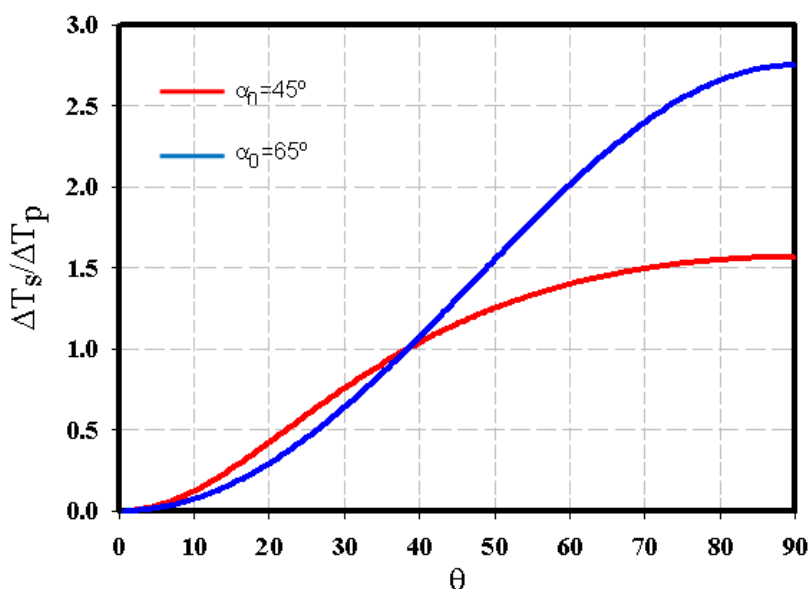


Figura 2.6. Representación de la relación dicróica $\Delta T_s/\Delta T_p$, vs θ a diferentes ángulos de incidencia α_θ . (Línea roja $\alpha_\theta = 45^\circ$ y línea azul $\alpha_\theta = 65^\circ$)

2.6. Determinación de la Orientación Molecular mediante Reflexión con Luz Polarizada y Ángulo Variable en la Interfase Aire-Agua

Una limitación de la técnica de reflexión de incidencia normal, empleada en el apartado 2.3 de esta Sección para calcular la fuerza del oscilador mediante la integración de la banda de reflexión, ecuación (2.18), deriva en que no puede aplicarse a bandas complejas formadas por dipolos de transición con diferentes orientaciones.⁶⁻⁷ Esta limitación ha sido de forma

general superada transfiriendo la monocapa de Langmuir a un soporte sólido, y analizando posteriormente la película mediante espectroscopía de transmisión con luz polarizada a distintos ángulos de incidencia, como se ha estudiado en el apartado anterior (2.5). Sin embargo la transferencia de una monocapa de Langmuir a un soporte sólido, puede alterar de forma significativa la organización molecular del sistema, no conservándose la estructura que había previamente en la interfase aire-agua.

Mediante el empleo de luz polarizada, a diferentes ángulos de incidencia, es posible resolver “in situ”, en la interfase aire-agua, bandas con diferente polarización, ya que al incidir con radiación p-polarizada a ángulos de incidencia mayores al ángulo de Brewster, podemos descomponer la banda en una parte positiva y otra negativa, en función de la polarización de sus componentes.

Para un material uniaxial y asumiendo que la película es isotrópica en el plano aplicamos la expresión (2.11) para hallar el factor de orientación. (ver Figura 2.7)

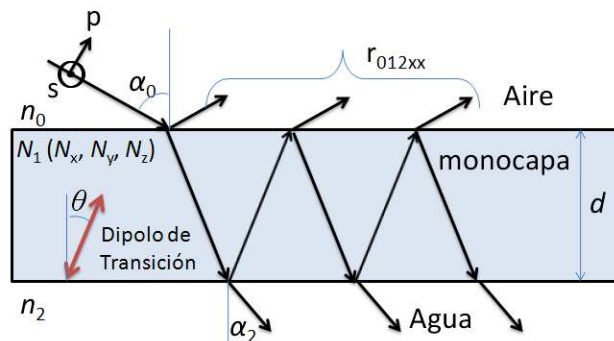


Figura 2.7. Ilustración de la reflexión de un sistema de tres capas, donde la capa cero es aire, la capa uno es la película depositada y el medio tres es la subfase, agua. La flecha negra representan la luz incidente y la flecha roja representa la dirección del dipolo de transición.

A partir de las ecuaciones de Fresnel para luz polarizada s y p, y en función del ángulo de incidencia α_0 , se pueden determinar los coeficientes de

reflexión para materiales biaxiales anisótropos en sustratos isotrópicos como aire o el agua.⁸

$$r_{01pp} = \frac{N_x N_z \cos(\alpha_0) - n_0 \left(N_z^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}}{N_x N_z \cos(\alpha_0) + n_0 \left(N_z^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}} \quad (2.34)$$

$$r_{12pp} = \frac{n_2 \left(N_z^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} - N_x N_z \cos(\alpha_2)}{n_2 \left(N_z^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} + N_x N_z \cos(\alpha_2)} \quad (2.35)$$

$$r_{01ss} = \frac{n_0 \cos(\alpha_0) - \left(N_y^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}}{n_0 \cos(\alpha_0) + \left(N_y^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}} \quad (2.36)$$

$$r_{12ss} = \frac{\left(N_y^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} - n_2 \cos(\alpha_2)}{\left(N_y^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} + n_2 \cos(\alpha_2)} \quad (2.37)$$

donde n_0 es el índice de refracción del aire, n_2 el índice de refracción del agua y N es el índice de refracción complejo para materiales anisotrópicos.

Los coeficientes de reflexión total vienen dados por la ecuación (2.38), siendo x la polarización s o p .

$$r_{012xx} = \frac{r_{01xx} + r_{12xx} \exp(-2 \cdot i \cdot \beta_x)}{1 + r_{01xx} r_{12xx} \exp(-2 \cdot i \beta_x)} \quad (2.38)$$

Los valores de β_p y β_s quedan definidos como:

$$\beta_p = \frac{2\pi d}{\lambda} \frac{N_x}{N_z} \left(N_z^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2} \quad (2.39)$$

$$\beta_s = \frac{2\pi d}{\lambda} \left(N_y^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2} \quad (2.40)$$

donde λ es la longitud de onda y d es el espesor de la película. Se puede obtener la Reflectancia para luz polarizada, siendo $x=s$ o p , mediante la siguiente relación:

$$R_x = |r_{012xx}|^2 \quad (2.41)$$

Los índices de refracción complejos para cada eje, (expresión (2.23)) en materiales anisotrópicos se definen mediante la siguiente expresión:

$$N_q = n_q - ik_q \quad (2.42)$$

donde $q \equiv x, y, z$, siendo n_q la parte real del índice de refracción y k_q la constante de absorción de cada eje. Esta expresión puede simplificarse si consideramos constante algunos valores $n_x = n_y = n_z = n_1$. Para poder aplicar esta aproximación se ha tenido en cuenta la relación de Kramers-Kroning,⁸ en la que se predice que la dispersión de la parte real de los índices de refracción es cero a la longitud de onda de máxima absorción. De esta forma, sólo se considera el valor de la reflexión a la longitud de onda de máxima absorción.

Si además se considera que el medio es isotrópico en el plano x - y (plano de la interfase), las constantes de absorción para cada eje quedan definidas mediante las siguientes expresiones:

$$\begin{aligned} k_x = k_y &= \frac{3}{2} k_{\text{iso}} \langle \sin(\theta)^2 \rangle = \frac{3}{2} k_{\text{iso}} P(\theta) \\ k_z &= 3k_{\text{iso}} \langle \cos(\theta)^2 \rangle = 3k_{\text{iso}} [1 - \langle \sin(\theta)^2 \rangle] = 3k_{\text{iso}} [1 - P(\theta)] \end{aligned} \quad (2.43)$$

donde k_{iso} es la constante de absorción en un medio isotrópico. Usando este modelo, la reflexión para una película a una longitud de onda λ , y ángulo de incidencia α_0 dado, depende de cuatro parámetros experimentales: índice de refracción n_1 , espesor de la película d , valor de la constante de absorción k_{iso} , y el parámetro de orden $P(\theta)$.

De la relaciones (2.43), puede obtenerse:

$$P(\theta) = 2k_x / k_z + 2k_x \quad (2.44)$$

De esta forma un valor de $P(\theta) = 0$, se corresponderá con un situación en la que el momento de transición sea perpendicular al plano x-y, donde $k_x=k_y=0$, y un valor de $P(\theta) = 1$, se corresponderá con una situación en la que el momento de transición sea paralelo al plano de la interfase ,donde $k_z=0$.

Si aplicamos estas ecuaciones (2.34-2.44) para $d = 2 \text{ nm}$, $n_1 = 1.55$, $k_{\text{iso}} = 0.5$, $P(\theta) = 0.8$, and $\lambda = 500 \text{ nm}$. Los valores de reflexión teórica ΔR_s y ΔR_p vs α_0 , de una película que tenga las características consideradas se observan en la Figura 2.8.

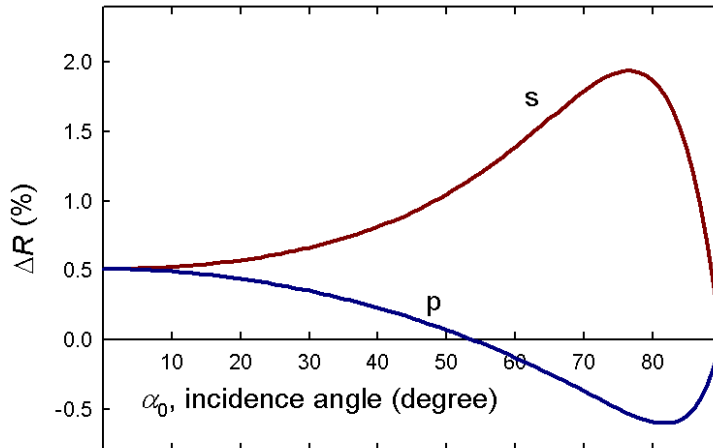


Figura 2.8. Gráfica de ΔR_s (línea roja) línea azul ΔR_p (línea azul) vs α_0 , siendo $d = 2 \text{ nm}$, $n_1 = 1.55$, $k_{\text{iso}} = 0.5$, $P(\theta) = 0.8$, and $\lambda = 500 \text{ nm}$.

Como puede observarse la reflexión s polarizada ΔR_s , es siempre positiva excepto para valores cercanos a 90° , mientras la reflexión p polarizada ΔR_p , puede ser positiva o negativa.⁹⁻¹⁰ La existencia de bandas negativas tiene lugar exclusivamente con luz p polarizada, y se da sólo en películas de espesores muy pequeños y a ángulos cercanos y mayores al ángulo de Brewster.

Como puede deducirse de las ecuaciones (2.34)-(2.43), las reflexiones ΔR_s and ΔR_n (reflexión a incidencia normal a la interfase aire-agua) dependen de las constantes de absorción $k_x = k_y$, componentes que se encuentran en el plano de la interfase aire-agua. De esta forma ΔR_s y ΔR_n no dependen de k_{iso} y $P(\theta)$ separadamente. Por tanto, el parámetro de orden $P(\theta)$ no puede obtenerse a través de ΔR_s y/o ΔR_n .

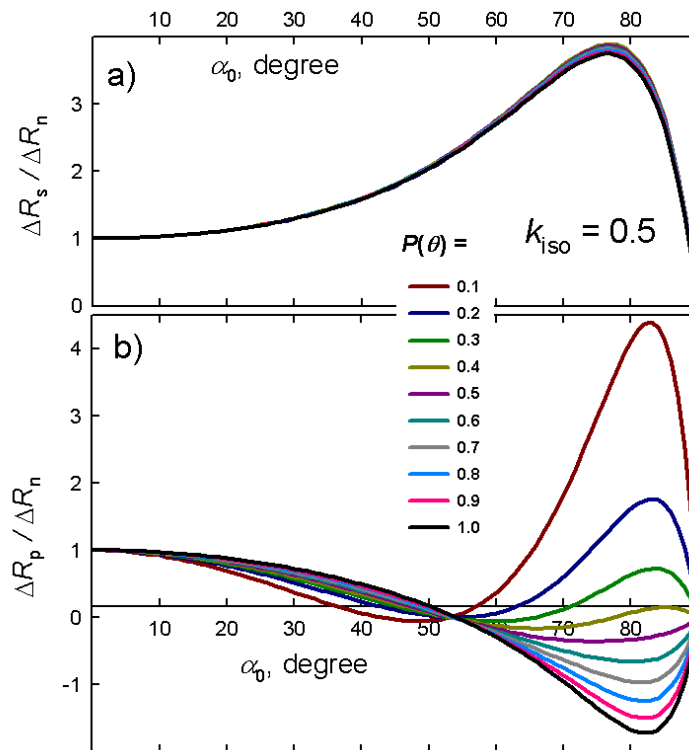


Figura 2.9. (a) Representación de $\Delta R_s/\Delta R_n$ y (b) $\Delta R_p/\Delta R_n$ frente α_0 , para $\lambda = 500$ nm, $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$. Los diferentes valores de $P(\theta)$ son indicados en la figura.

En la Figura 2.9 (a) se representa $\Delta R_s/\Delta R_n$ frente α_0 para $\lambda = 500$ nm, $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$, a diferentes valores de $P(\theta)$. Se observa que la relación $\Delta R_s/\Delta R_n$ es prácticamente independiente del valor de $P(\theta)$, lo que indica que las curvas no ofrecen información sobre la orientación de la

componente perpendicular (z) del dipolo, ofreciéndonos sólo información sobre la componente en el plano x - y .

En cambio la representación $\Delta R_p/\Delta R_s$ vs α_0 y en las mismas condiciones, Figura 2.9 (b), sí permite distinguir grandes variaciones del valor de $P(\theta)$ sobre todo a ángulos cercanos al ángulo de Brewster, y estas variaciones dependen de k_{iso} and $P(\theta)$, de forma independiente, permitiendo calcular el valor de $P(\theta)$.

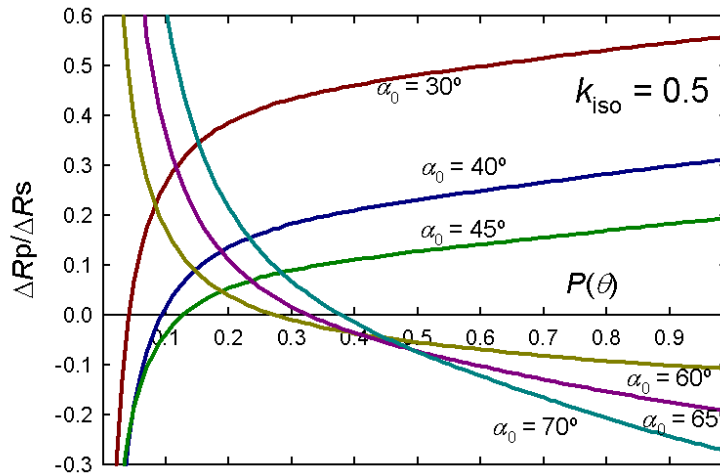


Figura 2.10. Curvas $\Delta R_p/\Delta R_s$ frente a $P(\theta)$, para para $\lambda = 500$ nm, $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$. Los diferentes ángulos de incidencia α_0 , son indicados en la figura.

Las curvas de las Figuras 2.9 y 2.10, no pueden usarse de forma general, ya que pueden conducir a errores en la estimación de $P(\theta)$, sólo se usan bajo ciertas condiciones como son: $d \leq 3$ nm, $1.75 \geq n_1 \geq 1.45$ y $1.5 \geq k_{iso} \geq 0.05$. Estos valores son típicos en monocapas de Langmuir.¹¹

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3. Agregación

3.1. Introducción

En esta sección se estudia la agregación molecular de forma general, aunque particularizando al estudio de agregados formados por cianinas y derivados, confinados en un medio 2D como la interfase aire-agua y las películas Langmuir-Blodgett (LB).

Se han seleccionado estos sistemas, cianina y derivados, como ejemplo de estudio de la agregación, ya que son algunos de los sistemas que han sido estudiados en esta Tesis, y desde el punto de vista histórico fueron no sólo las primeras moléculas en las que se observó el fenómeno de la agregación molecular, sino además uno de los sistemas más estudiados y que más publicaciones tiene en este campo.

En la década de los años 30 del siglo XX, Scheibe¹ y Jelley² de forma simultánea observaron los cambios en el espectro UV-Visible de una cianina en disolución acuosa al compararlo con el obtenido usando etanol como disolvente. Al cotejar los espectros, se ponía de manifiesto que el máximo de absorción se desplazaba a menores energías con etanol, y un comportamiento similar ocurría si se incrementaba la concentración de cianina o se añadía a la subfase cloruro sódico, haciéndose la banda más intensa y estrecha con grandes desviaciones de la ley de Lambert-Beer. Jelley and Scheibe atribuyeron los cambios en el espectro a la autoagregación del colorante cianina.

La mayor parte de las propiedades espectroscópicas de los agregados moleculares son consecuencia de las propiedades individuales de las moléculas. Sin embargo, a pesar de que en estos sistemas la energía de interacción entre las moléculas es débil, es posible observar grandes diferencias entre los espectros de absorción de la molécula aislada y del agregado molecular.

Hoy en día se conocen estos agregados como agregados Scheibe o agregados J, en honor a sus descubridores. Estos agregados J presentan bandas con altos coeficientes de absorción ϵ , y desplazadas hacia valores de

menor energía (batocrómicas) con respecto a la banda del monómero, así como propiedades fluorescentes con pequeños desplazamientos de Stokes.

En cambio los agregados con bandas de absorción desplazadas a mayores energías (hipsocrómicas) son los llamados agregados H, y en la mayoría de los casos no son fluorescentes. Los desplazamientos espectrales de los agregados H y J, indican que las propiedades moleculares individuales son alteradas por la agregación, formándose estados excitados coherentes debido al acoplamiento de los momentos dipolares de transición de cada molécula.

Estos cambios espectrales fueron interpretados por primera vez por Förster mediante el modelo del oscilador clásico,³ y después mediante la teoría de los estados excitados o teoría del excitón de Davydov,⁴ que se estudiará más detenidamente en el siguiente apartado. Posteriormente algunos autores como Kuhn y Dietz aplicaron métodos cuánticos para calcular el desplazamiento del espectro de cianinas para los H y J agregados.⁵

El descubrimiento de la agregación ha significado un gran hito en la química de los colorantes y el germen de la química supramolecular, otorgando a estos sistemas multitud de propiedades ópticas y fotoquímicas que han derivado en valiosas aplicaciones.⁶

3.2. Modelo de los Dipolos Extendidos

Cuando una molécula es excitada electrónicamente en el seno de un agregado molecular, dicho estado puede ser transportado a moléculas vecinas de forma que es compartido colectivamente, en mayor o menor medida, por el agregado. El hecho de que el estado excitado tenga cierta movilidad, permite introducir, como concepto teórico, la existencia de una *cuasi-partícula* asociada a dicho movimiento. A dicha *cuasi-partícula* se le denomina *excitón*. Los complejos de transferencia de carga, excímeros, polarones, bipolarones, y los denominados agregados H y J son, entre otros, ejemplos de *excitones*.⁷

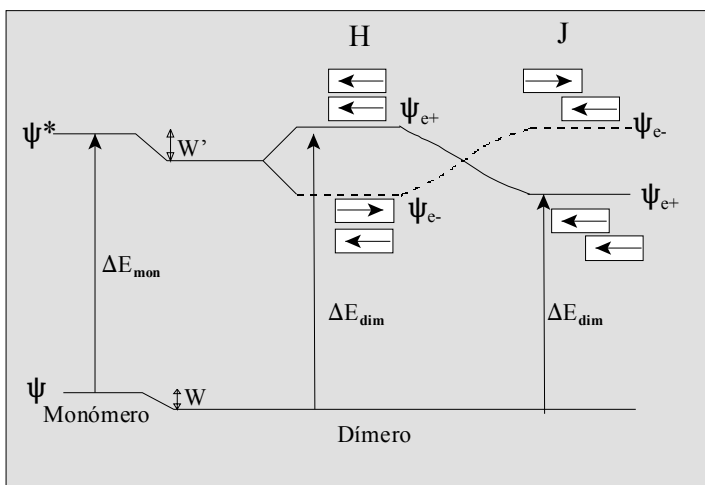


Figura 3.1. Representación de los niveles de energía y transiciones espectroscópicas para monómeros y dímeros H y J.

Supongamos una molécula aislada, siendo ψ y ψ^* las funciones de onda de su estado fundamental y de su primer estado excitado, respectivamente, y ΔE_{mon} la energía correspondiente a la transición espectroscópica entre ambos (parte izquierda de la Figura 3.1).

En el caso más simple, nuestro agregado estará formado solo por dos moléculas idénticas (dímero físico o de van der Waals). Si ψ_1 y ψ_2 son las funciones de onda fundamentales de estas moléculas, el producto $\psi_1\psi_2$ representará, de forma aproximada, la función de onda fundamental del agregado. Supongamos ahora que una de las dos moléculas es excitada electrónicamente, y que $\psi_1^*\psi_2$ y $\psi_1\psi_2^*$ representan estas dos opciones. En principio ambas moléculas tienen la misma probabilidad de ser excitadas y, de hecho, el estado excitado es compartido entre ambas. La función de onda de este estado excitado compartido (excitón), puede ser representada mediante una combinación lineal de las dos opciones anteriores. El método variacional de la Mecánica Cuántica nos enseña que, en estos casos, son posibles dos combinaciones lineales diferentes y, por lo tanto, dos estados excitados diferentes representados por las funciones:

$$\psi_{e\pm} = \frac{1}{\sqrt{2}} (\psi_1 \psi_2^* \pm \psi_2 \psi_1^*) \quad (3.1)$$

Si las dos moléculas interactúan mediante un operador energía V_{12} , las energías de los estados ψ_{e+} y ψ_{e-} dependen de la denominada integral de interacción resonante la cual tiene la forma:

$$J = \int \psi_1^* \psi_2 V_{12} \psi_2^* \psi_1 d\tau \quad (3.2)$$

por lo que la energía correspondiente a la transición espectroscópica en el dímero puede ser expresada mediante la relación,⁷

$$\Delta E_{\text{dim}} = \Delta E_{\text{mon}} + \Delta W + 2J \quad (3.3)$$

donde $\Delta W = W^e - W$ (ver Figura 3.1) da cuenta de las diferentes energías de interacción electrostáticas que puedan existir entre los estados excitados y fundamental de las moléculas. En este término se suelen incluir otras componentes no tenidas en cuenta, tales como fuerzas de dispersión y/o solapamiento entre orbitales. Sin embargo, y con frecuencia, este término suele despreciarse. El factor 2 que multiplica a J en la ecuación anterior procede del hecho de que el orbital HOMO está doblemente ocupado.⁸

La integral de la ecuación (3.2) representa la energía de interacción entre los dos momentos dipolares de transición, μ , de cada molécula. Este hecho permite evaluar dicha integral, de forma aproximada, sustituyéndola por su equivalente clásico, es decir, por la energía de interacción entre dos osciladores clásicos acoplados. El método consiste en suponer que cada molécula puede ser representada por su dipolo de transición μ , y que este puede ser expresado mediante la relación $\mu = q\ell$, donde q es la separación de carga y ℓ la longitud del dipolo formado (ver Figura 3.2). La energía de interacción entre las moléculas será por lo tanto:

$$J = \frac{q^2}{\epsilon} \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{a_3} - \frac{1}{a_4} \right) \quad (3.4)$$

donde ϵ es la constante dieléctrica del medio ($\epsilon \approx 2.5$), a_1 y a_2 representan las distancias entre cargas del mismo signo y, a_3 y a_4 las distancias entre cargas de signo opuesto, tal como se muestra en la Figura 3.2. La sustitución de la integral (3.2) por la expresión (3.4), constituye la base de la denominada aproximación de los *dipolos extendidos*.⁸

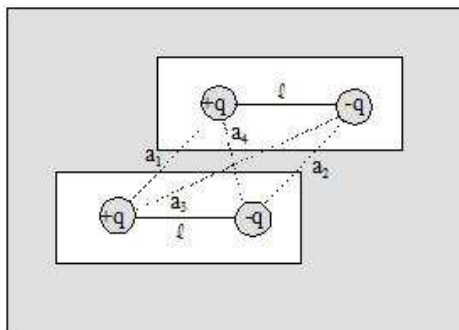


Figura 3.2. Interacciones electrostáticas entre las cargas de dos dipolos los cuales representan los dipolos de transición de dos moléculas.

Para $r \gg \ell$, siendo r la distancia entre los centros geométricos de las moléculas (ver Figura 3.3), es posible simplificar la ecuación anterior, ya que

$$q^2 \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{a_3} - \frac{1}{a_4} \right) \approx \frac{q^2 \ell^2}{r^3} = \frac{\mu^2}{r^3} \quad (3.5)$$

Esta expresión es válida para un ángulo $\theta = 0$. En general, para cualquier ángulo se cumple que (ver Figura 3.3):

$$J \approx \frac{\mu^2}{\epsilon r^3} \left(1 - 3 \cos^2(\theta) \right) \quad (3.6)$$

A su vez, la expresión anterior es la base de la denominada aproximación de los *dipolos puntuales*.⁹⁻¹⁰ Dada la sencillez de esta última, la utilizaremos como referencia para definir los conceptos de agregados H y J.

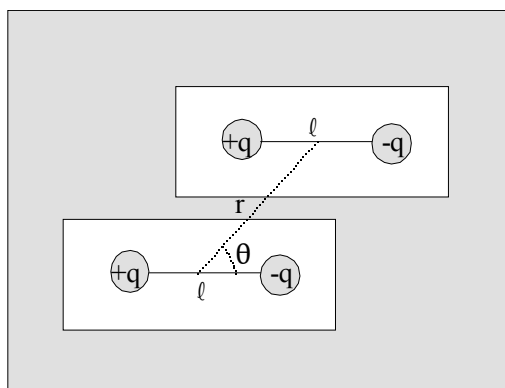


Figura 3.3. Esquema del desplazamiento de los dipolos de transición medio a través del ángulo θ .

Supongamos que el agregado (dímero) posee una estructura apilada en la que $\theta = 90^\circ$ (ver Figura 3.3). Esta estructura está representada, asimismo, en la parte central de la Figura 3.1, y será denominada agregado H. Si utilizamos el símil clásico, donde las moléculas pueden ser representadas por dipolos oscilantes, el estado ψ_{e+} correspondería a un acoplamiento paralelo de dichos osciladores. Es decir, las cargas positivas y negativas oscilan en el mismo sentido, lo que da lugar a una cierta energía de repulsión y, por lo tanto, a una situación de mayor energía que la correspondiente al monómero en estado excitado (ver Figura 3.1). Esta situación corresponde a un valor positivo de la integral J (ecuación 3.6).

Por el contrario, el estado ψ_{e-} corresponde a un acoplamiento antiparalelo en el que las cargas oscilan en sentido contrario, lo que da lugar a una situación de menor energía (integral J negativa). Puesto que el dipolo de transición del agregado es suma de los correspondientes a los monómeros, la resultante para ψ_{e-} es cero, lo que significa que este estado no es activo desde el punto de vista espectroscópico y, por lo tanto, no da lugar a banda de absorción. Este hecho es mostrado en la Figura 3.1 mediante línea discontinua. Hay que indicar que esto es cierto sólo si las moléculas están orientadas en la misma dirección, en caso contrario los dos estados, ψ_{e+} y ψ_{e-} , serían activos.

Una característica, por lo tanto, de los agregados H, es que la banda

de absorción tiene lugar a mayor energía que la del monómero (desplazamiento hacia el azul, ver Figura 3.1).

Supongamos ahora que el dímero posee una estructura en la que $\theta \rightarrow 0^\circ$ (ver Figura 3.3). Esta estructura es representada a la derecha de la Figura 3.1, y será denominada agregado J. En este caso, las energías de los estados electrónicos se invierten con respecto a la situación anterior. En efecto, cuando el acoplamiento de los osciladores es paralelo (estado ψ_{e+}), estos se atraen, lo que da lugar a una cierta disminución de la energía (integral $J < 0$). Por el contrario, cuando el acoplamiento es antiparalelo (estado ψ_{e-}), los osciladores se repelen, dando lugar a un aumento de energía (integral $J > 0$). Es decir, la principal característica de los agregados J es que su banda de absorción tiene lugar a menor energía que la del monómero.

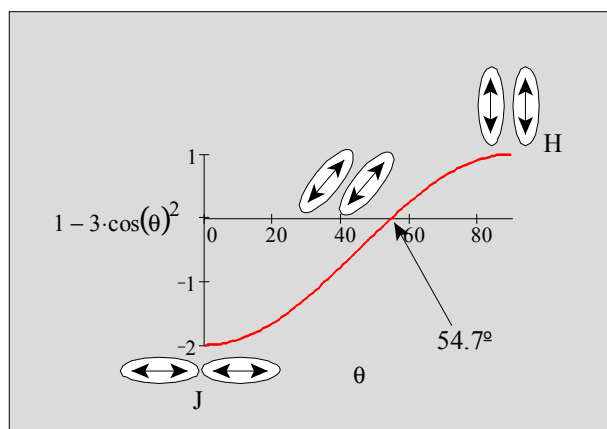


Figura 3.4. Representación de $1-3\cos(\theta)^2$ vs θ y su influencia en el tipo de agregado.

La transición entre un agregado H y J puede ser analizada de una forma simplificada a través de la ecuación (3.6). En la Figura 3.4, se representa la función $1-3\cos(\theta)^2$ vs θ . Esta función es cero para $\theta = 54.7^\circ$, por lo que teóricamente a este ángulo, no debe de existir desplazamiento en la banda de absorción del dímero con respecto al monómero (suponiendo $\Delta W = 0$ en la ecuación 3.3). Para $\theta > 54.7^\circ$ dominan las fuerzas de repulsión y el agregado es H, mientras que para $\theta < 54.7^\circ$ dominan las fuerzas de atracción y

el agregado es J.

La definición anterior de agregados H y J, en base al modelo de dipolos puntuales, está limitada al cumplimiento de la relación $r \gg \ell$. El empleo de la ecuación (3.6) de forma generalizada, en sustitución del modelo de los dipolos extendidos (ecuación 3.4), puede conducir a errores considerables en la interpretación de los resultados. En la Figura 3.5, se muestra un ejemplo de esta afirmación. En la parte izquierda de esta figura se representan los planos de las moléculas y sus centros geométricos separados una distancia b y d , respectivamente. Con estas consideraciones, y suponiendo que la longitud del dipolo es ℓ , es posible definir:

$$r = a_1 = a_2 = \sqrt{b^2 + d^2} \quad (3.7) \qquad \theta = ar \cos\left(\frac{d}{r}\right) \quad (3.8)$$

$$a_3 = \sqrt{(\ell + d)^2 + b^2} \quad (3.9) \qquad a_4 = \sqrt{(\ell - d)^2 + b^2} \quad (3.10)$$

Suponiendo que ℓ y b son conocidos, y dando valores a su vez al parámetro d , es posible calcular r (ecuación. 3.7), θ (ecuación. 3.8), así como todas las distancias a_i . De esta forma, es posible determinar la relación $J\ell/q^2$, ya sea según el modelo de los dipolos extendidos (ecuación. 3.4) o el de los dipolos puntuales (ecuación. 3.6).

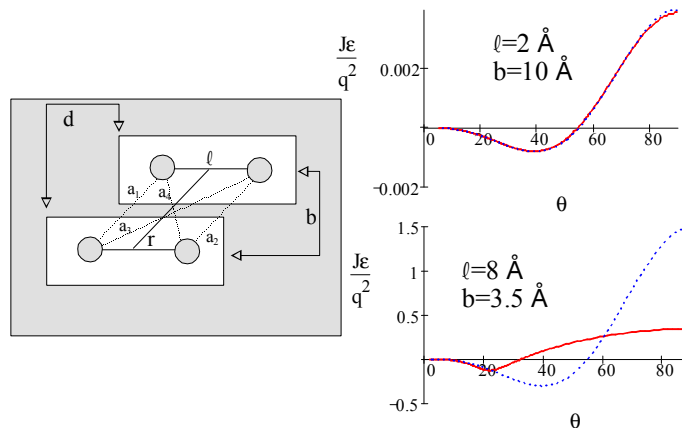


Figura 3.5. Diagrama de los dipolos de transición de dos moléculas (parte izquierda), aplicación del modelos de dipolos puntuales (línea azul de puntos), y dipolos extendidos (línea roja continua), para dos valores de ℓ y b .

En la parte derecha de la Figura 3.5 se muestran dos ejemplos de aplicación de las anteriores expresiones. Así, cuando $l = 2 \text{ \AA}$ y $b = 10 \text{ \AA}$, los valores de $J\mathcal{E}/q^2$ para el modelo de los dipolos puntuales (línea azul de puntos) y de los dipolos extendidos (línea roja continua) coinciden prácticamente, como cabe esperar de la relación $r > \ell$.

Sin embargo, cuando $l = 8 \text{ \AA}$ y $b = 3.5 \text{ \AA}$, valores que están dentro del rango de los encontrados experimentalmente,^{8,11} la variación de $J\mathcal{E}/q^2$ para ambos modelos es muy diferente. En concreto, la transición entre agregados H y J se sigue produciendo en el modelo de los dipolos puntuales (línea azul de puntos) a un ángulo de $\theta = 54.7^\circ$, mientras que en el modelo de los dipolos extendidos (línea roja continua) dicha transición tiene lugar a $\theta = 31.9^\circ$. Es decir, en este caso, el modelo de los dipolos puntuales no es capaz de predecir correctamente las regiones en las que dominan las fuerzas atractivas y repulsivas entre dipolos. Asimismo, el modelo de los dipolos puntuales exagera la energía de repulsión entre dipolos.

En la Figura 3.5 se observa como $J\mathcal{E}/q^2$ tiende a cero, cuando θ tiende a cero. En realidad $\theta = 0^\circ$ sólo cuando $d = \infty$ y, por lo tanto, la energía de interacción entre dipolos es cero.

Aparte de las ventajas obvias del modelo de los dipolos extendidos, tiene sin embargo, un inconveniente práctico que hace que este modelo haya sido poco utilizado. En efecto, a partir de la integración de la banda de absorción del monómero en disolución, es posible determinar el valor del módulo del momento dipolar de transición μ , pero no los valores de q y l por separado. La determinación de estos valores necesita de un dato experimental adicional, este es, el desplazamiento de la banda de absorción para un agregado de estructura conocida.

En cualquier caso, la aplicación cuantitativa de ambos modelos necesita del conocimiento previo de algunos parámetros estructurales del agregado, como es la separación entre los planos moleculares. Con frecuencia dicha estructura solo puede ser conocida mediante espectros de difracción de

rayos X, si bien, en ocasiones, puede obtenerse información estructural a partir de otros tipos de experimentos. Así, por ejemplo, la determinación de áreas superficiales en la interfase aire-agua en unión con los propios datos espectroscópicos, permite, en situaciones favorables, deducir dicha información, o a través de simulación con mecánica molecular.

Para analizar un ejemplo supongamos que, para un determinado cromóforo se observa que el máximo de su banda de absorción se desplaza desde $\lambda_{\text{mon}} = 351$ nm, para el monómero, hasta $\lambda_{\text{dim}} = 339$ nm para el dímero. Supongamos además que la integración de la banda del monómero en disolución ha permitido obtener que $\mu = q \cdot l = 2.56 \cdot 10^{-29}$ C·m = 7.7 D. A partir de la ecuación (3.3), y suponiendo que $\Delta W = 0$, es posible calcular:

$$J = \frac{hc10^7}{2} \left(\frac{1}{\lambda_{\text{dim}}} - \frac{1}{\lambda_{\text{mon}}} \right) = 10^{-13} \text{ erg} \quad (3.11)$$

Si suponemos que la geometría del dímero es similar a la mostrada en la Figura 3.5, es posible combinar las ecuaciones (3.4), (3.7)-(3.10) de forma que,

$$J = \frac{\mu^2}{\ell^2 \epsilon} \left[\frac{2}{\sqrt{b^2 + d^2}} - \frac{1}{\sqrt{(\ell + d)^2 + b^2}} - \frac{1}{\sqrt{(\ell - d)^2 + b^2}} \right] \quad (3.12)$$

Si b y d son conocidas, la ecuación anterior posee una sola incógnita, la longitud del dipolo, l , la cual puede ser determinada numéricamente. Así, cuando $b = 4$ Å y $d = 0$, se obtiene, para el ejemplo anterior, $l = 5.73$ Å y $q = 0.278 e$, donde e representa la carga de un electrón.

El estudio de las propiedades espectroscópicas de agregados de orden N , puede efectuarse mediante un procedimiento similar al descrito con anterioridad.¹¹ En sustitución de la ecuación (3.3) es posible escribir que:¹¹⁻¹²

$$\Delta E_N = \Delta E_{\text{mon}} + \Delta W + \frac{2}{N} \sum_{i \neq j} J_{i,j} \quad (3.13)$$

donde ΔE_N representa la energía del salto espectroscópico para el agregado de orden N , y $J_{i,j}$ es la energía de interacción entre los dipolos de transición de dos moléculas i y j cualesquiera del agregado. Los valores de $J_{i,j}$ pueden determinarse a partir de la ecuación (3.4). El sumatorio de la ecuación (3.13) está extendido a todas las posibles parejas de moléculas del agregado, de forma que, la energía de interacción total es promediada al dividir por N . Por ejemplo, en el caso del dímero ($N=2$), $(2/N)\sum J_{i,j} = (2/2) (J_{1,2} + J_{2,1}) = 2J$, como ya se conoce de la ecuación (3.13).

Supongamos que el agregado está formado por trímeros apilados. La ecuación (3.13) conduce a:

$$\Delta E_3 = \Delta E_{\text{mon}} + \Delta W + \frac{2}{3} (J_{1,2} + J_{1,3} + J_{2,1} + J_{2,3} + J_{3,1} + J_{3,2}) \quad (3.14)$$

Evidentemente si la estructura es apilada, las interacciones entre moléculas contiguas serán todas iguales, luego $J_{1,2} = J_{2,1} = J_{2,3} = J_{3,2}$, mientras que $J_{1,3} = J_{3,1}$, luego:

$$\Delta E_3 = \Delta E_{\text{mon}} + \Delta W + \frac{2}{3} (4J_{1,2} + 2J_{1,3}) = \Delta E_{\text{mon}} + \Delta W + \frac{8}{3} J_{1,2} + \frac{4}{3} J_{1,3} \quad (3.15)$$

En general, para una estructura apilada de N agregados, puede deducirse que,

$$\Delta E_N = \Delta E_{\text{mon}} + \Delta W + \frac{2}{N} [J_{1,2} 2(N-1) + J_{1,3} 2(N-2) + J_{1,4} 2(N-3) + \dots] \quad (3.16)$$

donde el subíndice 1 representa una molécula de referencia. En cualquier caso, la ecuación anterior no está completa ya que, se ignoran las interacciones laterales entre pilas contiguas de moléculas. Si solo se tienen en cuenta las interacciones entre moléculas contiguas ($j = i \pm 1$) y, se supone que $N = \infty$, la ecuación anterior se reduce a la ecuación

$$\Delta E_{\infty} = \Delta E_{\text{mon}} + \Delta W + 4J_{1,2} \quad (3.17)$$

que ha sido utilizada con frecuencia para analizar el desplazamiento de las bandas de absorción en agregados de orden infinito.

El modelo de los dipolos extendidos ha sido utilizado en el desarrollo de los Capítulos III y IV para analizar la organización molecular de los sistemas de cianina y quinoleína en películas superficiales.

3.3. Espectro UV-Visible de las Cianinas y sus Agregados

Las cianinas, son colorantes que se clasifican en base a la longitud de la cadena cromófora que conecta los dos heterociclos aromáticos,¹³⁻¹⁴ siendo n el número total de grupos meteno (CH) _{n} de la cadena (ver Figura 3.6).

Se denomina cianina aquella que tiene un único grupo meteno ($n=0$), y carbocianina a la que presenta tres grupos meteno ($n=1$), dicarbocianina y tricarbocianina las que contienen cinco ($n=2$) y siete ($n=3$), respectivamente.

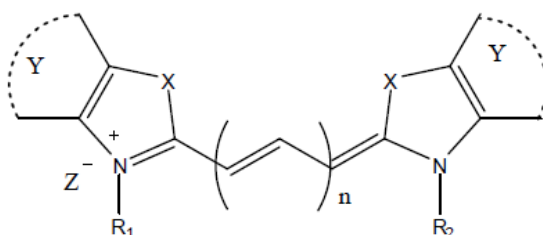


Figura 3.6. Estructura y clasificación de las cianinas: $n=0$ - cianina; $n=1$ - carbocianina; $n=2$ - dicarbocianina y $n=3$ - tricarbocianina. $X = \text{S, Se, O, N, ...}$; $Y =$ Grupos de heterociclos terminales como benzotiazol o benzooxazol; $Z^- = \text{Cl}^-, \text{ClO}_4^-, \dots$

Los heterociclos aromáticos dador (D) y aceptor (A) de cada molécula de cianina se conectan a través de la cadena alquílica, alternando enlaces simples y dobles, y simultaneando la densidad electrónica π entre los átomos de carbono, como se muestra en la figura 3.7. La gran fuerza del oscilador de la cadena de polimeteno provoca el pronunciado color.

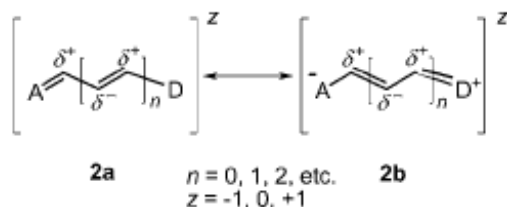


Figura 3.7. Estructura de la cadena de polimeteno, donde se muestra la densidad de carga positiva y negativa, respectivamente.

El espectro UV-visible del monómero de la tiacarbocianina en disolución, muestra una intensa banda de la transición electrónica $0 \rightarrow 0$, ($S_0 \rightarrow S_1$) siendo esta transición fundamentalmente del tipo, $\pi \rightarrow \pi^*$ y un hombro a mayor energía que está relacionado con las transiciones vibracionales de la molécula, esencialmente a las vibraciones C-C.⁶

La posición de la banda principal del espectro UV-visible de la cianina, además de los factores ambientales como disolvente, pH, presencia de electrolitos, presencia de aditivos como alcoholes y ácidos, depende del número de grupos metenos conjugados que hay entre los dos heterociclos; así la banda aparecerá a una mayor longitud de onda a medida que se incrementa el número de grupos metilenos, n (Tabla 3.1).¹⁵

n	λ_{max} (nm)	ϵ_{max} ($M^{-1} \text{cm}^{-1}$)
0	423	$83 \cdot 10^3$
1	558	$168 \cdot 10^3$
2	650	$235 \cdot 10^3$
3	758	$251 \cdot 10^3$

Tabla 3.1. Serie de absorción de la 3,3'-Dietil-2,2'- tiocianina en etanol.

Aunque el espectro UV-visible del monómero de cianina puede modificarse por factores ambientales y estructurales, los cambios más sustanciales en el espectro se deben al efecto de la agregación, produciéndose la aparición de nuevas bandas hacia mayores y menores longitudes de onda con respecto al monómero.

Como se ha descrito en el apartado anterior, un agregado formado por moléculas de monómero, será activo desde el punto de vista espectroscópico y, por tanto tendrá absorción, si el sumatorio de los dipolos de transición de las moléculas de monómero que lo forman es diferente de cero. Los dipolos de transición de las moléculas de monómero que forman el agregado pueden alinearse de forma paralela o perpendicular, pasando por los diferentes ángulos de alineación entre ellos, y formando los agregados H y J entre otros.

Estos agregados pueden formarse espontáneamente en disolución cuando se incrementa la concentración, o a través de las películas de Langmuir confinados en un medio 2D, y formando estructuras de diferente número de moléculas, que pueden ir desde las más simples (dímeros), a grandes estructuras formados por 10^3 - 10^6 moléculas.¹⁶

El número de unidades de monómero que forma el agregado, es decir la longitud coherente del excitón, es mucho menor que el tamaño del dominio formado, así el número de unidades de monómero sobre las que se deslocaliza la función de onda del excitón (longitud coherente del excitón), no suele superar el número varias decenas de unidades monoméricas, aunque algunos estudios demuestran que la migración del excitón en algunos sistemas y en ciertas condiciones de temperatura, puede migrar a través de 6×10^4 - 6×10^6 unidades monoméricas,¹⁷ en cualquier caso es muy pequeña en comparación con el tamaño del dominio. De esta forma pueden existir dominios macroscópicos formados por agregados moleculares de diferente longitud coherente, dando lugar a espectros complejos con múltiples bandas, como los agregados tubulares de doble capa que se forman en disolución y dan lugar a un espectro complejo de cuatro bandas de absorción,¹⁸ o los descritos en el Capítulo IV de esta memoria. De esta forma, sistemas formados en distintas condiciones de pH y con diferentes sales en el medio, dan lugar a dominios con morfología diferente, pero con el mismo espectro de absorción, lo que demuestra que aunque la morfología de los dominios macroscópicos no se conserve, presentan la misma agregación a escala molecular.

Si tomamos como ejemplo un agregado formado por moléculas anfífilas confinados en un medio 2D, como la interfase aire-agua, si sus dipolos de transición no son paralelos en el agregado, tanto la componentes H como la J pueden ser activas, dando lugar a un desdoblamiento o "splitting" de la banda, y apareciendo una estrecha banda perteneciente a un agregado J, y una banda más ancha correspondiente al agregado H,¹⁹ con diferentes propiedades de polarización. Así, pueden existir tantas bandas en el espectro como moléculas no equivalentes existan por celda unidad, según el modelo de Davydov.^{7,20} El estudio de estas bandas con diferente polarización en la interfase aire-agua, se puede realizar in situ con la técnica de Reflexión de ángulo variable (Capítulo IV de la presente memoria).

También pueden observarse diferentes agregados J en el mismo sistema, los cuales pueden ser identificados por: 1) la posición de la banda J en el espectro; 2) la anchura de la banda de absorción y fluorescencia; 3) el valor del desplazamiento de Stokes; y 4) la forma del espectro de absorción.²¹ Esto ocurre en sistemas no homogéneos, donde debido a las condiciones experimentales o de preparación, se forman varios dominios con estructuras y tamaños coherentes diferentes.²²

Otra forma de estudiar los diferentes agregados J que se pueden formar en el sistema, y sobre la base de que estos agregados presentan distintos tiempos de decaimiento, es mediante la espectroscopía de tiempo resuelto, la anisotropía de fluorescencia o el dicroísmo lineal.

De otra parte, la morfología de los agregados depende sensiblemente de la estructura molecular de los sustituyentes,²³ así por ejemplo se han observado agregados de cianinas anfífilas en disolución que con sutiles cambios estructurales en los sustituyentes hidrofóbicos o hidrofílicos derivan en diversas formas de agregados tubulares.²⁴ Estos pequeños cambios en la estructura de la molécula, también les aporta propiedades distintas a las cianinas, como la ausencia de fluorescencia.

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4. Quiralidad

4.1. Introducción y Conceptos

La palabra quiral proviene de la palabra griega "cheir", que significa mano. Nuestras manos son simétricas pero no son superponibles: la mano derecha es la imagen especular de nuestra mano izquierda, pero el guante de una mano no sirve para la otra. En la naturaleza, diversos objetos macroscópicos como las manos, los órganos de los animales, los organismos biológicos, las macromoléculas y algunos objetos microscópicos como las moléculas son quirales. La quiralidad es una consecuencia de la geometría molecular: aquellas moléculas que presentan un plano de simetría (σ) o un centro de simetría (τ) son aquirales (sin quiralidad), mientras que aquellas moléculas que no presentan dichos elementos de simetría son necesariamente quirales, y no son superponibles con su imagen en el espejo.¹

La quiralidad es condición necesaria y suficiente para la existencia de los enantiómeros o isómeros ópticos, es decir, compuestos cuyas moléculas tienen la misma fórmula molecular y la misma secuencia de átomos enlazados, con los mismos enlaces entre sus átomos, pero difieren en la orientación tridimensional de sus átomos en el espacio, (estereoselectividad) (Figura 4.1).

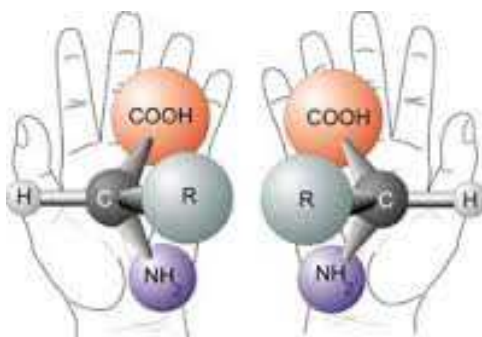


Figura 4.1. Muestra de dos estructuras isoméricas de un aminoácido cualquiera, constituyen un par de enantiómeros.

Cabe destacar que los enantiómeros, presentan las mismas propiedades físicas excepto la interacción con la luz polarizada en un plano: un isómero desvía el plano de polarización hacia la derecha, mientras el otro isómero lo desvía en la dirección contraria. También presentan las mismas propiedades químicas, excepto cuando reaccionan con otros agentes quirales.

Los diastereoisómeros, son isómeros configuracionales no enantioméricos, y en contraste con la situación anterior entre pares enantioméricos, los diastereoisómeros siempre presentan propiedades físicas y reactividad diferente. Esta diferencia en el comportamiento de enantiómeros y diastereómeros es muy útil en el desarrollo de metodologías que conducen a la separación de mezclas o a la síntesis enantioselectiva de compuestos quirales.

Como se ha dicho anteriormente, una propiedad de las moléculas quirales, es que rotan el plano de luz polarizada. Cuando un haz de luz polarizada atraviesa una molécula quiral su plano se rota siempre debido a la interacción de la luz polarizada con la tendencia relativa de la distribución de carga de las moléculas, es decir la polarizabilidad, pues la luz al interactuar con las partículas cargadas pierden una cantidad de energía haciendo que la dirección de propagación de la luz se desvíe: la orientación de la luz y la magnitud de la rotación varían con la orientación de la molécula particular en el haz, la distribución electrónica y en el caso de las moléculas quirales con la presencia de centros de simetría.

En una muestra de un enantiómero puro, ninguna molécula puede servir como imagen especular de otra: no hay anulación de rotaciones y el resultado neto es la actividad óptica. En cambio, una mezcla racémica con una proporción equimolecular de enantiómeros, daría una distribución cuyo resultado neto es igual a cero, es decir sin actividad óptica. Así, en una sustancia compuesta por moléculas quirales, por cada molécula que la luz atraviesa hay otra (idéntica) orientada como imagen especular de la primera lo que cancela el efecto. El resultado neto es la ausencia de rotación de la luz polarizada, es decir, la inactividad óptica, de modo que esta no es una propiedad de las moléculas individuales, sino más bien de la distribución al

azar de moléculas que pueden servir de imágenes especulares recíprocas. Por tanto, la actividad óptica es una propiedad física que permite distinguir los isómeros ópticos, y es que los isómeros ópticos desvían el plano de vibración de la luz polarizada en sentidos opuestos. El polarímetro es por tanto un instrumento básico para trabajar con isómeros ópticos o enantiómeros (Figura 4.2).

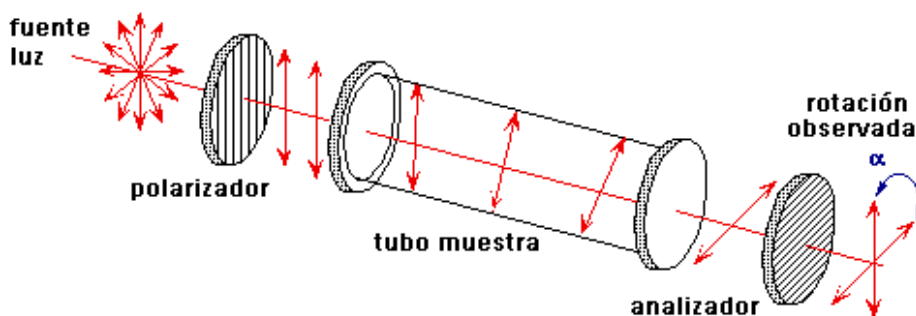


Figura 4.2. Esquema de un polarímetro.

El polarímetro es un instrumento mediante el cual podemos determinar el valor de la desviación de la luz polarizada por un estereoisómero ópticamente activo (enantiómero). La polarimetría es una técnica que se basa en la medición de la rotación óptica producida sobre un haz de luz polarizada al pasar por una sustancia ópticamente activa. Un rayo de luz atraviesa un polarizador obteniéndose un rayo de luz polarizada plana, que al pasar por un portamuestras que contiene un enantiómero en disolución, se desvía. La luz polarizada pasará por un segundo polarizador según la orientación relativa entre los ejes de los dos polarizadores. Si esto es así, la luz llegará al detector con un cierto ángulo indicando la desviación de la luz polarizada (Figura 4.2). Si la sustancia que contiene un enantiómero tiene la propiedad de hacer girar el plano de la luz polarizada hacia la izquierda, el enantiómero se denomina levógiro (L). En el caso de que la sustancia haga girar el plano hacia la derecha, se denominará dextrógiro (D).

4.2. Quiralidad Supramolecular en un Plano

La definición anteriormente dada de quiralidad sólo tiene en cuenta el estudio de moléculas quirales, es decir que difieren en la orientación tridimensional 3D de sus átomos en el espacio. Estas moléculas son las que tienen algún átomo de carbono asimétrico.

Sin embargo, los sistemas que se estudian en esta Memoria están confinados en un medio bidimensional 2D, bien sea formando una película en la interfase aire-agua, o una monocapa transferida a un soporte sólido.

En química, el concepto de crear estructuras quirales a partir de moléculas aquirales o la combinación de moléculas quirales y aquirales, es llamado quiralidad supramolecular, este término se utiliza para describir conjuntos supramoleculares que no son superponibles sobre sus imágenes especulares en el espacio tridimensional o en un plano 2D.²⁻³

Los sistemas quirales 2D, consisten en agregados de moléculas quirales o proquirales, donde la quiralidad es inducida por el confinamiento de las moléculas a una superficie 2D. Estos agregados forman ensamblajes supramoleculares mediante enlaces no covalentes, donde las moléculas quirales o proquirales se organizan de una manera no simétrica para producir una “superestructura” que es quiral, dando lugar a la quiralidad supramolecular.⁴

Desde un punto de vista físico se define un sistema quiral como aquel que es capaz de discriminar luz polarizada circularmente. La luz polarizada circularmente se puede producir por la superposición de dos haces de luz que están oscilando perpendicularmente entre sí y propagándose con una diferencia de fase de $\pi/2$ radianes. La magnitud del vector del campo eléctrico del haz de luz resultante es constante, pero gira alrededor de la dirección de propagación. Si el vector forma una hélice dextrógira, se refiere a una luz polarizada circularmente a la derecha, mientras que si el vector forma una hélice levógira se refiere a una luz polarizada circularmente a la izquierda.

Los sistemas quirales tienen la propiedad de poseer índices de refracción diferentes para la luz polarizada circularmente dextrógira y

levógira, es decir, los haces de luz viajan a diferentes velocidades y son absorbidos en diferentes grados dependiendo de cada energía. Esto significa que los coeficientes de extinción molar para la luz circularmente polarizada dextrógira y levógira son diferentes, $\epsilon_L \neq \epsilon_R$. Este efecto se llama Dicroísmo Circular DC.

La absorbancia diferencial, $\Delta\epsilon$, de la luz polarizada circularmente a la derecha y a la izquierda se representa frente a la longitud de onda λ para producir el espectro DC:

$$\Delta\epsilon = \epsilon_L - \epsilon_R \quad (4.1)$$

La integral de $\Delta\epsilon$ en un rango de longitud de onda asociada con una transición particular se conoce como la fuerza de DC o fuerza rotacional de esa transición. La fuerza rotacional, R_{ba} , de una transición desde un estado fundamental a un estado excitado es el producto del momento dipolar de la transición eléctrica $\bar{\mu}$, y el momento dipolar de la transición magnética \bar{m} . La combinación de $\bar{\mu}$ por \bar{m} crea un desplazamiento de carga helicoidal, dando lugar a una interacción diferente con luz polarizada circularmente a la izquierda y a la derecha. La fuerza rotacional en unidades de $\text{erg}\cdot\text{cm}^3$ se define experimentalmente como:

$$R_{ba} = \frac{3000 \ln(10) hc}{32\pi^3 N_A} \int \frac{\Delta\epsilon(\bar{\nu}) d\bar{\nu}}{f \cdot \bar{\nu}} = 0.248 \int \frac{\Delta\epsilon(\bar{\nu}) d\bar{\nu}}{f \cdot \bar{\nu}} \quad (4.2)$$

donde h es la constante de Planck, N_A es el número de Avogadro, n el índice de refracción, ν la frecuencia y $f = (n^2 + 2)/3$, es la corrección de campo local.

L. Rosenfeld, definió en 1928 la fuerza rotacional, R , como la parte escalar del producto de los momentos de transición del dipolo magnético m_{ba} , y del eléctrico, μ_{ba} , de la siguiente forma:

$$R_{ba} = -\text{Im}(\langle \Psi_b | \bar{m} | \Psi_a \rangle \cdot \langle \Psi_b | \bar{\mu} | \Psi_a \rangle) = -\text{Im}(m_{ba} \cdot \mu_{ba}) \quad (4.3)$$

donde Ψ_a y Ψ_b indican las funciones de onda del estado fundamental y excitado, respectivamente, e Im la parte imaginaria del producto.

La fuerza de rotación R_{ba} , va a depender por tanto de la medida en que los dipolos de transición magnéticos y eléctricos cooperan o se oponen entre sí. De forma más precisa R_{ba} será distinto de cero (y por tanto habrá quiralidad) sólo si m_{ba} y μ_{ba} tienen componentes que son paralelas o antiparalelas. Esto implica que un sistema tendrá quiralidad siempre y cuando sus dipolos de transición magnéticos m_{ba} y eléctricos μ_{ba} no sean perpendiculares entre sí. Los sistemas supramoleculares quirales en un plano que cumplen estas condiciones suelen estar formados por moléculas que tienen algún tipo de disposición helicoidal, como los mostrados en la Figura 4.3.



Figura 4.3. Ejemplo de mecanismo de ensamblaje supramolecular. Los anillos aromáticos de las moléculas están inclinados en el mismo plano que sus moléculas vecinas, formando un ensamblaje supramolecular con una disposición en espiral en el plano, y dando lugar a dos estructuras no superponibles.

4.3. Importancia de la Quiralidad en Biología y en Química

La mayoría de las moléculas biológicas presentes en la naturaleza son quirales, los aminoácidos que forman las proteínas son de la forma L, mientras que la ribosa y la desoxirribosa, los azúcares que forman parte del esqueleto de los ácidos ribonucleicos, el ARN y el ADN respectivamente, son de la forma D. ¿Por qué la naturaleza es quiral? Aunque esto es todavía un gran enigma, una posible explicación es que si la evolución molecular, se basara en una “vida racémica” sería mucho menos favorable que la ruta evolutiva que da lugar a la “vida homóquiral”. Este hecho se interpreta fácilmente si se piensa que sólo tiene actividad biológica el isómero que se acopla perfectamente con su receptor. Efectivamente, se puede argumentar

que si los procesos biológicos operaran de forma racémica, serían mucho más complicados, ya que los organismos estarían forzados a utilizar dos o más conjuntos de enzimas (receptores). El funcionamiento de tales organismos sería mucho más complejo que el sistema con un solo conjunto de enzimas.⁵

Debido al continuo interés de la quiralidad en biología, desde el punto de vista de la química, se ha estudiado con gran detalle la estructura cristalina y propiedades físicas de los enantiómeros y de las mezclas racémicas. De ahí que sea vital la capacidad de producir los enantiómeros separadamente.⁶ Y precisamente esta producción selectiva de moléculas quirales ha sido objeto del premio Nobel de Química (2001) para S. Knowles, R. Noyori y B. Sharpless.

El desarrollo de la síntesis catalítica asimétrica es de enorme importancia para la investigación científica, pero sobre todo para el desarrollo de nuevos fármacos y otras sustancias biológicamente activas.

Para ello, se propone el empleo de catalizadores con moléculas quirales, que facilitan la producción de un enantiómero frente al otro sin consumirse en el proceso. Una sola molécula de catalizador puede producir dependiendo de su función como tal, de las condiciones y de la reacción en sí, una gran cantidad de moléculas del enantiómero deseado.

William S. Knowles descubrió que era posible utilizar metales de transición para producir catalizadores quirales para un importante tipo de reacciones orgánicas, las de hidrogenación, obteniendo así un rendimiento más elevado de uno de los enantiómeros. Su investigación industrial llevó a la producción de la L-DOPA, un medicamento utilizado en el tratamiento de la enfermedad de Parkinson.⁷ Ryoji Noyori desarrolló este proceso hasta generalizarlo para las reacciones quirales de hidrogenación.⁸⁻⁹ Por su parte, K. Barry Sharpless desarrolló catalizadores quirales para procesos de oxidación.¹⁰⁻¹¹

Mediante estos estudios se ha revelado una correlación interesante entre quiralidad y funcionalidad tanto a niveles microscópicos como macroscópicos en los sistemas biológicos. Sin embargo, lo más importante es

que estas unidades biológicas pierden funcionalidad cuando sus estructuras quirales se alteran, en la mayoría de los casos, sólo un enantiómero es biológicamente activo. Un ejemplo muy significativo de la capacidad de la selectividad de los sistemas biológicos es el limoneno, una molécula quiral cuyos enantiómeros son indistinguibles en los procesos químicos corrientes, pero que nuestro olfato discrimina con facilidad porque se acoplan a receptores distintos. Así, el isómero (R)-limoneno huele a naranjas, mientras que el (S)-limoneno huele a limones.¹²

En otras ocasiones, los isómeros quirales tienen resultados biológicos más dramáticos, de vida o muerte. Es el caso de la talidomida, que en los años sesenta se prescribió a las mujeres embarazadas porque uno de sus enantiómeros tenía capacidad para evitar las náuseas. Desgraciadamente, se descubrió más tarde que el otro enantiómero de la talidomida provocaba deformaciones en el feto.

Entender la preferencia quiral mostrada por la naturaleza también tiene aplicaciones prácticas, así los fármacos enantioméricos constituyen >30% de la drogas terapéuticas totales utilizados en los últimos años. Y constituyen > 50% de las ventas totales, como fármacos cardiovasculares, hormonales, antibióticos, antifúngicos. En consecuencia, un mejor entendimiento sobre la orientación y la dependencia distancia-interacción debido a la estructura quiral de las moléculas en los sistemas biomiméticos y biomoleculares será de utilidad en el diseño de nuevos fármacos que tengan una función más eficaz.¹³

4.4. Quiralidad en Interfases Modelo

En los últimos años ha tenido un especial interés los trabajos relacionados con los proceso de reconocimiento quiral en la interfase aire-agua, así han surgido trabajos donde se pone de manifiesto el reconocimiento o discriminación quiral entre los componentes de la monocapa entre sí, y entre los componentes que forman la monocapa con compuestos huésped de la subfase (guest-host).

La discriminación quiral entre los componentes que forman una monocapa conduce a la separación de los isómeros y a la formación de estructuras ordenadas.³ En el segundo caso, guest-host, la discriminación de una monocapa formada por moléculas quirales, como isómeros puros, implica que sólo ciertas moléculas huésped de la subfase puedan ser albergadas por la monocapa. Así anfífilicos quirales como lípidos o azúcares son capaces de discriminar incluso a pequeños iones, de forma similar a lo que ocurre con las membranas lipídicas de nuestro organismo.¹⁴

La quiralidad en sistemas supramoleculares en la interfase aire-agua, puede ser generada a través de ensamblar moléculas quirales, moléculas aquirales, o una combinación de ambas,¹⁵ también mediante fenómenos de coordinación con iones o ensamblaje de moléculas aquirales mediante una matriz aquiral.¹⁶

Existen muchos trabajos de investigación dedicados de una forma tanto práctica como teórica al estudio de los compuestos quirales y su inclusión en el diseño y fabricación de dispositivos moleculares, objetivo básico de la Química Supramolecular y de la Nanotecnología. De esta forma se han usado moléculas quirales anfífilicas como las derivadas del 1,1'-Binaftilo en catálisis enantioselectiva heterogénea, y en la fabricación de sensores de discriminación quiral.¹⁷⁻¹⁸

Gracias a la técnica de Langmuir y las técnicas espectroscópicas empleadas para el estudio "in situ" de las monocapas, o la caracterización mediante la técnica de Dicroísmo Circular de las películas transferidas por la técnica de Langmuir-Blodgett o Langmuir-Schaefer, se puede discriminar compuestos quirales o enantiómeros puros frente a una mezcla racémica.

Por ejemplo, la medida de las isothermas presión superficial-área (π -A) ayudan a distinguir los enantiómeros (dextrógiro o levógiro) frente a la mezcla racémica, pues las isothermas difieren en las áreas por molécula y las presiones de colapso alcanzadas.¹⁹⁻²⁰ Las isothermas de los enantiómeros son menos expandidas que las correspondientes a la mezcla racémica de los

mismos en ciertas condiciones de pH y temperatura, así varía su forma, teniendo lugar la transición de fases a distintas presiones.

También se conoce que la cinética de relajación a presión constante de monocapas formadas por enantiómeros puros es más rápida que la formada por la mezcla racémica de los mismos.²¹

El estudio de la morfología de la monocapa mediante la técnica de microscopía de ángulo de Brewster (BAM), permite observar las grandes diferencias existentes entre la morfología de los enantiómeros puros y de una mezcla racémica de los mismos. La diferencia estriba en la dirección de crecimiento de los dominios: el enantiómero dextrógiro crece en sentido de las agujas del reloj mientras que el enantiómero levógiro crece en sentido contrario (Figura 4.5). Sin embargo, la mezcla racémica puede crecer en ambas direcciones, o puede cancelar el efecto de rotación, originando dominios con brazos rectos, como ocurre con la mezcla racémica del DPPC. Con ayuda de éstas técnicas, se pueden proponer modelos moleculares que establecen distintas conformaciones de los agregados en la monocapa.^{3,22-25}

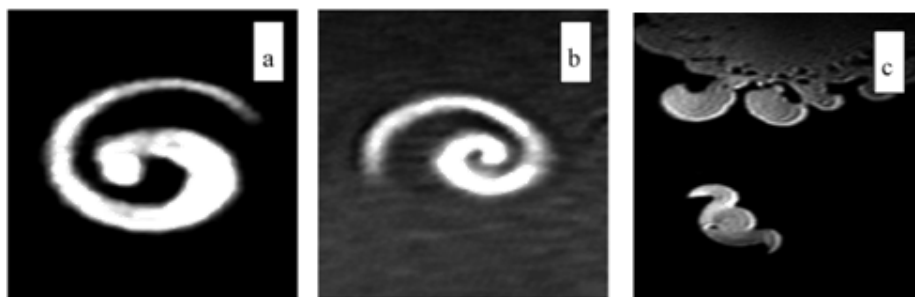


Figura 4.5. Discriminación quiral de N-estearoilserinamilester en monocapas de Langmuir: a) D-enantiómero, b) L-enantiómero, c) mezcla DL-racémica en proporción 1:1.¹³

La presencia de distintos haluros en la subfase, así como la temperatura y velocidad de barrido, determina el tamaño, curvatura y forma de los dominios. Por ejemplo, en función del haluro en la subfase, se han observado dominios con forma de espiral o forma de pájaro formados por L-Glutamato.²⁶

Asimismo, es de interés la creación de un sistema molecular quiral a través de especies (moléculas o iones) no quirales. Se puede preparar una monocapa de Langmuir esparciendo un anfifílico, por ejemplo derivados de imidazoles, en agua pura y al cambiar la subfase, añadiendo una concentración de un ión, por ejemplo Ag (I), se observan cambios importantes en las características de la monocapa. En la isoterma presión-área aparece un cambio de fase que anteriormente no existía. El espesor y la morfología también se ven modificados. Usando técnicas espectroscópicas, se detectan cambios más espectaculares, especialmente en espectroscopia infrarroja y UV-vis, por ejemplo, en dicroísmo circular (DC) aparecen picos en presencia del ión, cuando en ausencia del mismo no existen. Este efecto da cuenta de la quiralidad producida al coordinarse el ión con el anfifílico. Este resultado es crucial, pues no sólo identifica la quiralidad del sistema, sino que aporta importantes claves para el diseño y fabricación de ensamblajes moleculares quirales, a partir de compuestos aquirales.^{2,27-28}

También se han formado dominios con geometría aquiral, pero con textura interna quiral a través de mezclas de fosfolípidos con actividad óptica y colorantes proquirales, como la formada por L-DMPA y hemicinanina. Las moléculas proquirales, no tienen actividad óptica, pero muestran quiralidad cuando está confinada en un medio 2D, como la interfase aire-agua. Así, sólo es posible una de las dos estructuras isoméricas, formándose dominios circulares con forma de S en su interior y en una única dirección.¹⁵

Por otra parte, también se ha estudiado la interacción quiral de forma teórica para intentar describir la morfología de los dominios. Como ejemplo de ello, se han empleado ácidos grasos para los que se utilizan cálculos de energía y variación de la posición alrededor del dominio. Con ello, se pretende relacionar el potencial del par intermolecular de un par de moléculas quirales, las cuales dependen de la separación entre ellas y la orientación azimutal de ambas, tomándose el centro quiral de las moléculas como referencia. De esta manera, se observa que la interacción es favorable si la orientación azimutal es del mismo tipo que la orientación de la molécula, y

por otra parte, la energía obtenida en la interacción entre las cabezas polares es del mismo orden de magnitud que la interacción por puente de hidrógeno. Este estudio es útil para entender la interacción molecular de compuestos quirales.²⁹

En el Capítulo IV de esta Memoria, se presenta el estudio mediante BAM los dominios quirales del sistema MQ:DMPA, observándose una gran variedad de formas y tamaños. Las distintas formas y tamaños son consecuencia de dos mecanismos diferentes de crecimiento del núcleo en la formación del dominio. Así, experimentalmente y a través de un control cinético, es posible minimizar el crecimiento de uno de estos mecanismos, logrando una distribución homogénea de los dominios.³⁰

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Capítulo II

Experimental



1. Técnicas de Formación y Caracterización de Monocapas en la Interfase Aire-agua.

1.1. Balanza de Langmuir

Los registros de isothermas presión superficial-área (π - A) y las curvas de estabilidad de área frente al tiempo, a presión superficial constante, constituyen el primer paso en la caracterización de una monocapa de Langmuir. Para la realización de las citadas experiencias se emplea la balanza de Langmuir. Este instrumento consta básicamente de los siguientes elementos: una cuba de teflón, donde se aloja el líquido que constituye la subfase (normalmente agua ultrapura MilliQ o una disolución acuosa), y sobre el que se esparce la disolución que contiene el material que va a formar la película; una barrera móvil o dos que separa la superficie de trabajo (donde se esparce la película) de la superficie limpia, y que es la encargada de comprimir la monocapa; y un sistema de medición de presión superficial. La velocidad de compresión utilizada en las diferentes isothermas oscila entre 0.05-0.1 nm²/min·molécula.

El sistema de medida de presión superficial de las balanzas de Langmuir empleadas en esta Memoria fue del tipo Wilhelmy.¹ El dispositivo experimental de este sistema está constituido por una lámina metálica, o de papel, que se encuentra parcialmente sumergida en la subfase y conectada, por el otro extremo, a una microbalanza electrónica de alta sensibilidad. De los tres tipos de fuerza a los que se encuentra sometida la lámina, peso, empuje y tensión superficial, sólo esta última varía por la presencia de la monocapa sobre la subfase respecto de la subfase limpia. Por tanto, la diferencia entre la fuerza medida antes y después de esparcir la monocapa es debida únicamente a la diferencia de tensión superficial, que es precisamente la presión superficial. En la Figura 1.1 se muestra un esquema de la balanza de Langmuir tipo Wilhelmy. En esta Memoria se han utilizado dos balanzas comerciales NIMA de tipo rectangular, modelos 611D y 601BAM, con una y dos barreras móviles respectivamente.

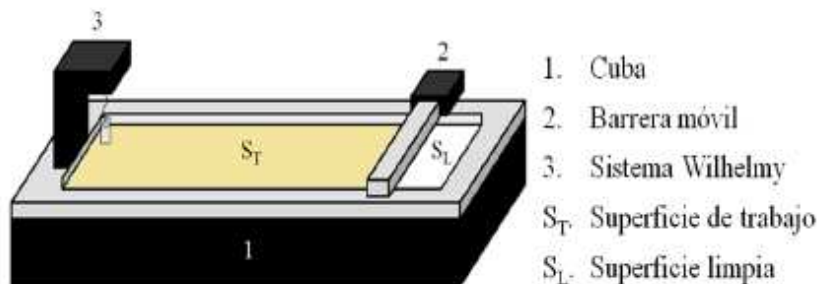


Figura 1.1 Esquema de una balanza de Langmuir tipo Wilhelmy.

1.2. Espectroscopía de Reflexión bajo Incidencia Normal

Las medidas de reflexión (ΔR), bajo incidencia normal, en la interfase aire-agua se han realizado en un equipo diseñado por *Nanofilm* (actualmente *Accurion GmbH*, www.accurion.com, Göttingen, Alemania), modelo RefSpec².

Como se describió en el Capítulo I de esta memoria, la espectroscopía de reflexión es una técnica muy útil en el estudio de monocapas en la interfase aire-agua,²⁻⁴ ya que registra la reflexión producida por las moléculas que se encuentran en dicha interfase y que contribuyen a resaltar su reflexión. La reflexión en la interfase aire-agua se mide como la diferencia de reflexión producida por la parte de la interfase cubierta con la monocapa respecto a la reflexión de la subfase limpia registrada antes de esparcir la monocapa.

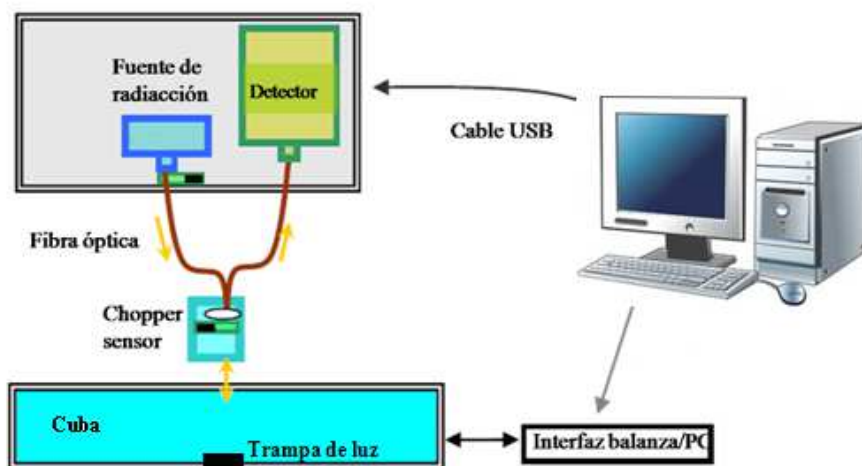


Figura 1.2. Esquema del reflectómetro RefSpec².

En la Figura 1.2 se puede ver un esquema de funcionamiento del espectrofotómetro de reflexión.³⁻⁴ La fuente de luz consiste en dos lámparas, una de deuterio y otra de tungsteno, ambas instaladas en un soporte de cerámica. La luz sale por una ventana de cristal de cuarzo, que la colima hacia la fibra óptica. Posteriormente esta radiación pasa por un monocromador instalado en el sensor. De ahí sale e incide en la superficie limpia o con muestra, esparcida sobre la interfase aire-agua. Este mismo sensor enfoca la luz reflejada hacia una fibra óptica, para que llegue al detector. Existen dos choppers que permiten alternar entre la radiación emitida por la lámpara y la reflejada por la muestra, ambos controlados electrónicamente. El chopper del sensor tiene su parte trasera cubierta por un espejo de forma que, además, sirve como referencia estática para las oscilaciones de la lámpara. En el fondo de la balanza se coloca una placa negra que actúa como trampa de luz para absorber los rayos transmitidos (ver Figura 1.2). De esta forma, la radiación reflejada entra al detector CCD, que envía la señal al ordenador donde se registra y procesa adecuadamente.

1.3. Espectroscopía de Reflexión Ultravioleta-Visible Bajo Incidencia Variable y Luz Polarizada

Los espectros de reflexión UV-visible bajo incidencia variable y luz polarizada se han realizado usando un equipo Refspec2VA (suministrado por Accurion GmbH).

Como se puede ver en la Figura 1.3, este equipo está acoplado a una balanza de Langmuir para realizar medidas “in situ” de la interfase aire-agua. El equipo dispone de un goniómetro motorizado para seleccionar ángulos de incidencia de 38-70 grados, con una resolución de 0.001 grados y una precisión de 0.01 grados. Dispone de un sistema de analizadores y polarizadores motorizados que le permite seleccionar las polarizaciones s y p. Tiene una lámpara de Xe con un rango espectral de 240-980 nm, y una resolución espectral de 3 nm.

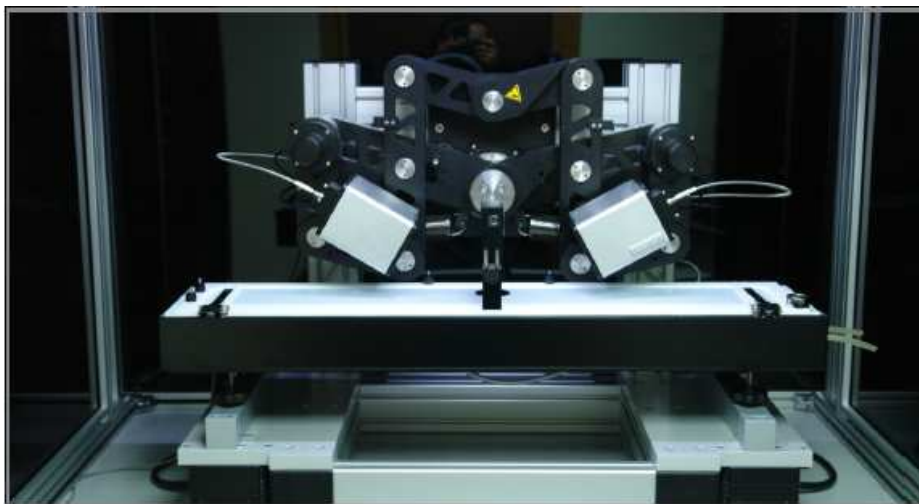


Figura 1.3. Imagen Espectroscopio de reflexión de ángulo variable acoplado a la balanza de Langmuir, y situado sobre una mesa antivibratoria.

Tanto el equipo como la balanza están situados sobre una mesa antivibratoria *Halcyonics (Accurion)* dentro de una cámara limpia.

1.4. Microscopía de Ángulo Brewster (BAM)

Las imágenes de microscopía de ángulo Brewster han sido obtenidas en un sistema comercial I-Elli2000 de *Nanofilm* (actualmente *Accurion*, www.accurion.com). El montaje experimental del microscopio BAM,⁵⁻⁶ representado en la Figura 1.4, se halla acoplado a una balanza de Langmuir donde se extiende la monocapa objeto de estudio.

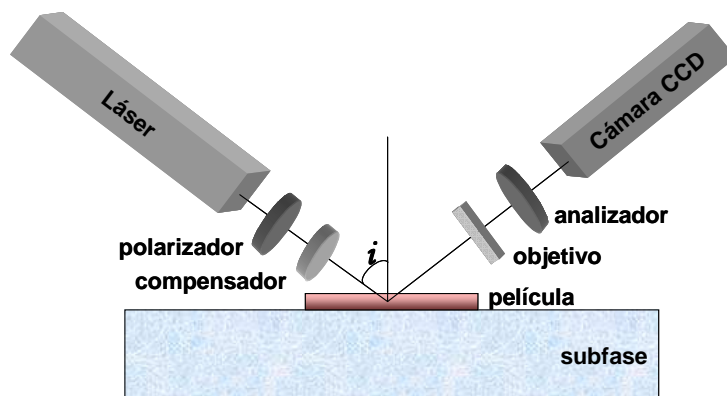


Figura 1.4. Esquema del Microscopio BAM.

El dispositivo se compone de un láser verde (Nd:YAG, 50 mW, 532nm) que produce un rayo de luz de 1.3 mm de diámetro, el cual atraviesa un polarizador, donde adquiere polarización p , e incide posteriormente sobre la interfase con $i = 53.15^\circ$, ángulo de Brewster para el agua. En este sistema, la intensidad de luz refractada es absorbida por una placa negra (trampa de luz) colocada en el fondo de la balanza, mientras que la reflejada pasa a través de un objetivo con distancia focal de 20 mm y llega a una cámara CCD de alta sensibilidad, que recoge la reflectividad debida a la presencia de la monocapa en la interfase. La resolución lateral del sistema óptico en el plano de la superficie acuosa es de 2 μm . La cámara CCD es capaz de registrar en forma electrónica la intensidad y el punto de llegada de pequeñísimas cantidades de luz, que son convertidas a imágenes de mapa de bits (768 x 562 píxeles), para su representación y análisis a través de la aplicación informática que controla el equipo. El procesamiento de la imagen incluye la corrección geométrica de ésta, así como el uso de filtros para reducir interferencias y ruido. Asimismo, el brillo de la imagen es reescalado para mejorar el contraste.

El microscopio está equipado con un analizador frente a la cámara que permite observar los posibles efectos ópticos de anisotropía en el interior de los dominios en que se organizan las moléculas que forman la película. De este modo, mediante la rotación del analizador respecto a la dirección de polarización p , luz incidente, se pueden observar diferencias en el contraste dentro de un mismo dominio, fenómeno indicativo de una diferente orientación molecular. Tanto el microscopio como la balanza están situados sobre una mesa antivibratoria *Halcyonics* (*Accurion*, www accurion.com) MOD-2 S, dentro de una cámara limpia. En la Figura 1.5 se muestra una imagen del instrumento utilizado.



Figura 1.5. Imagen del Microscopio BAM.

1.5. Difracción y Reflectividad de Rayos X

Las medidas de difracción de rayos X de incidencia rasante (GIXD) y las de reflectividad especular de rayos X (XRR) en la interfase aire-agua, fueron realizadas en la línea BW1 del HASYLAB (DESY, Hamburgo, Alemania). Las monocapas fueron preparadas en una balanza de Langmuir con una barrera móvil, termostatzada a 21°C, equipada con un dispositivo Wilhelmy como sensor de presión, y situada en un contenedor cerrado herméticamente y lleno de helio. En la línea BW1, un haz de rayos X sincrotrón monocromático ($\lambda=1.304 \text{ \AA}$), se ajusta para que incida en la interfase helio-agua con un ángulo rasante de $\alpha_i=0.85\alpha_c$ ($\alpha_c\approx 0.13^\circ$) e ilumine aproximadamente $2\times 50 \text{ mm}^2$ de superficie. Durante las medidas, la balanza se mueve lateralmente para evitar que la potente radiación X provoque daños en la muestra. Un detector sensible a la posición lineal (PSD, MYTHEN, Suiza) es girado en torno a la balanza para escanear los valores de la componente en el plano Q_{xy} del vector de dispersión. Los canales verticales del mismo detector sirven para medir la componente fuera del plano Q_z del vector de dispersión entre 0 y 0.8 \AA . La intensidad de la radiación detectada se corrige

en función de la polarización, el área efectiva y el factor de Lorentz. Los datos obtenidos para Q_{xy} y Q_z se ajustan por mínimos cuadrados a curvas modelo, Lorentzianas y Gaussianas, respectivamente. La intensidad de radiación difractada en dirección normal a la interfase es integrada en el rango del pico de difracción Q_{xy} para calcular la correspondiente “barra de Bragg”.

Para las medidas de reflectividad especular se usó el mismo dispositivo que para las medidas de difracción, pero siendo los ángulos incidente y reflejado iguales y variando en el rango $0.5 \alpha_c < \alpha_i$ (α_r) $< 30 \alpha_c$, y usando un detector de centelleo de NaI para medir la luz reflectada en el plano del rayo incidente, en función del vector de dispersión fuera del plano Q_z . El perfil de densidad electrónica fue obtenido de los datos de reflectividad, usando el método de aproximación de Pedersen y Hamley con el software StochFit.⁷

1.6. Espectroscopía Infrarroja de Reflexión y Absorción con Modulación de la Polarización (PM-IRRAS)

Los espectros de PM-IRRAS se han realizado usando el instrumento KSV PMI 550 (KSV NIMA, Espoo, Finland) equipado con un detector MCT. La descripción del procedimiento experimental del PM-IRRAS se ha presentado en el Capítulo I de esta Memoria.⁸ En la Figura 1.6, se muestra un esquema del instrumento.⁹

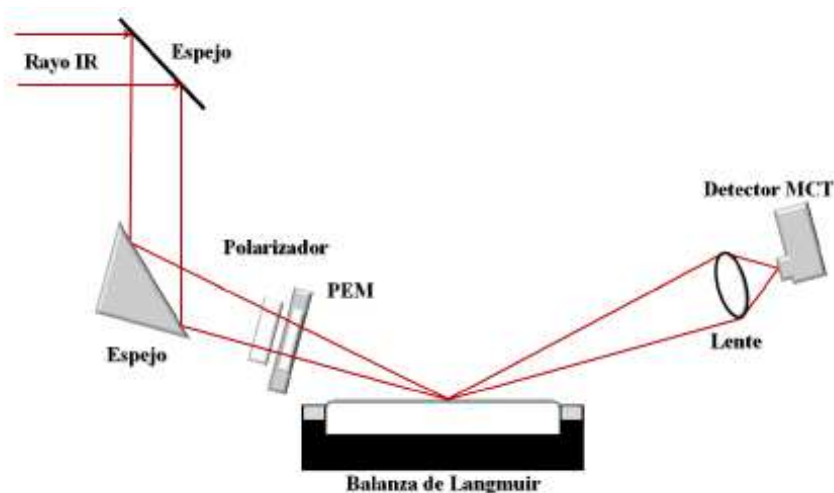


Figura 1.6. Esquema del PM-IRRAS.

La configuración consiste en una fuente de luz infrarroja, un interferómetro de Michelson y una unidad externa que capta la reflexión desde la balanza con la subfase y la monocapa. La intensidad de radiación infrarroja fue modulada por el interferómetro y polarizada por un polarizador de ZnSe. Una vez el rayo ha pasado a través del modulador fotoelástico de ZnSe, este modula el rayo en su componente paralela al plano de incidencia (p) y en su componente perpendicular al plano de incidencia (s) con una frecuencia fija de 100 kHz. Se obtienen dos señales: $(R_p - R_s)$ y $(R_p + R_s)$, de la intensidad detectada usando un filtro electrónico y un desmodulador de la señal. Sólo la absorción anisotrópica contribuye a la señal $S \approx (R_p - R_s)/(R_p + R_s)$ del PM-IRRAS. Las señales normalizadas fueron obtenidas directamente a través de la expresión siguiente: $\Delta S = (S_d - S_o)/S_o$, donde S_d y S_o son las señales registradas en presencia y en ausencia de monocapa. Para las experiencias realizadas en esta Memoria, el ángulo de incidencia del rayo infrarrojo con respecto a la normal a la interfase fue de 80° . Los espectros se obtuvieron con una resolución espectral de 8 cm^{-1} , usando 3000-6000 scans durante 5-10 min. En la Figura 1.7 se muestra una imagen del instrumento utilizado.



Figura 1.7. Imagen del PM-IRRAS.

2. Técnicas de Caracterización de Películas en la Interfase Aire-Sólido

2.1. Transferencia de Monocapas a Sustratos Sólidos

La transferencia de monocapas a soportes sólidos desde la balanza de Langmuir, se realizan mediante las técnicas de Langmuir-Blodgett (LB) y Langmuir-Schaeffer (LS). En el primer caso, se llevó a cabo por medio de un brazo mecánico acoplado a la balanza, que se mueve perpendicularmente a la interfase y que es controlado por ordenador. Los principales parámetros a tener en cuenta en la transferencia son la relación de transferencia, así como la velocidad a la cual ésta se lleva a cabo. La velocidad de transferencia osciló entre 5 y 10 $\text{mm}\cdot\text{min}^{-1}$. La fabricación de multicapas se realizó mediante la inmersión y/o emersión sucesiva del soporte en la monocapa mantenida en la interfase aire-agua a presión superficial constante.

En el caso de las películas LS las transferencias se realizaron mediante deposición horizontal (toque del soporte sobre la interfase aire-agua donde se encuentra la película).

Por último, indicar que los soportes empleados fueron vidrio o cuarzo.

2.2. Espectroscopia de Absorción UV-Visible

Los espectros de absorción UV-visible se obtuvieron en un espectrofotómetro Varian Cary 100 Bio. Los soportes de vidrio y cuarzo cubiertos con la monocapa transferida se colocaron en el paso de luz, situando un soporte de vidrio o cuarzo limpio, respectivamente, como referencia. Los espectros realizados con luz polarizada p y s se llevaron a cabo interponiendo entre la fuente de luz y el soporte un polarizador de la casa comercial Harrick, bajo diferentes ángulos de incidencia. Los datos obtenidos a partir de estos espectros nos ayudan a inferir la orientación de la molécula sobre el soporte¹⁰.

Así mismo, este equipo ha sido empleado para obtener los espectros de las disoluciones utilizadas en este trabajo, tanto acuosas como orgánicas, empleando cubetas de cuarzo Hellma de paso óptico 2 mm o 1 cm.

2.3. Dicroísmo Circular (DC)

Los espectros de Dicroísmo Circular (DC) se obtuvieron usando el espectropolarímetro Jasco J-71S CD, y fueron realizados en el laboratorio de bionanoplasmónica del CIC biomaGUNE (San Sebastián, España). Las monocapas fueron transferidas a un soporte de cuarzo limpio por la técnica de Langmuir-Schaefer, los espectros fueron medidos en un intervalo de longitud de onda de 280-700 nm, con una resolución de 0.2 nm y un ancho de banda de 1 nm. La velocidad del scan fue de 20 nm/min con 2 s de tiempo de respuesta. La descripción detallada del fundamento físico del DC está descrita en un Capítulo I.3 de esta Memoria.

En la figura 1.8, se muestra un esquema del instrumento.

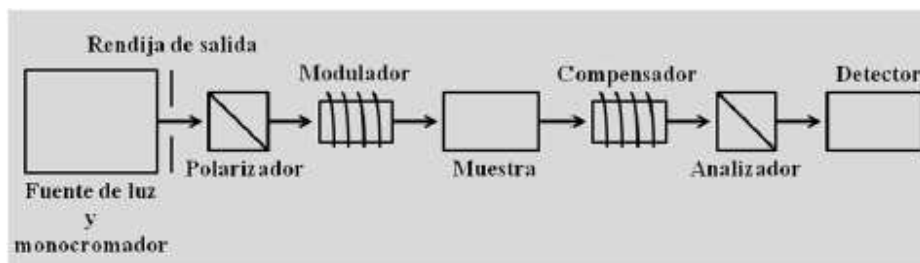


Figura 1.8. Esquema de un espectropolarímetro de Dicroísmo circular. Adaptado de *Métodos ópticos de análisis*; Olsen, E. D., Ed. Reverté 1990.

La característica más importante de un espectropolarímetro de Dicroísmo Circular (Figura 1.8),¹¹ es que debe contar con una fuente de luz polarizada. La fuente, inmóvil, debe ser lo más intensa posible de forma que maximice la relación señal/ruido. Generalmente es luz policromática. Normalmente, se utiliza una lámpara de carburo de silicio como fuente de radiación. La luz polarizada circularmente puede ser construida a partir de dos haces de luz polarizada linealmente que tengan la misma magnitud pero que estén fuera de fase una respecto a la otra. La luz pasa a través de un polarizador lineal que está orientado a 45° del retardador de onda. Se elige un retardador de espesor tal que los dos haces emergentes estén desfasados en $\pi/2$ cuando lo atraviesen, de manera que ambos constituyan luz circularmente polarizada hacia la derecha. Si el polarizador se rota 90°, la luz es circularmente polarizada hacia la izquierda. La luz polarizada pasa por un modulador fotoelástico que consiste en un material que se comprime y expande para producir radiación circularmente polarizada (generalmente un cristal de seleniuro de zinc) la cual incide sobre la muestra objeto de estudio, colocada en una celda con ventanas de materiales estables. La radiación que emana de la celda pasa a un detector que proporciona los espectros de dicroísmo circular.

2.4. Espectroscopía de Fluorescencia

Los espectros de excitación y emisión de fluorescencia, se obtuvieron usando un fluorímetro modelo FS920 Steady State Fluorimeter, (EdinburghInstrument, Livingston, UK). Este espectrómetro posee como fuente de radiación una lámpara pulsada de Xenon, además permite variar las anchuras de las rendijas de ambos monocromadores (excitación y emisión) y se pueden incorporar filtros para absorber la radiación a diferentes longitudes de onda, como se muestra en la Figura 1.9.

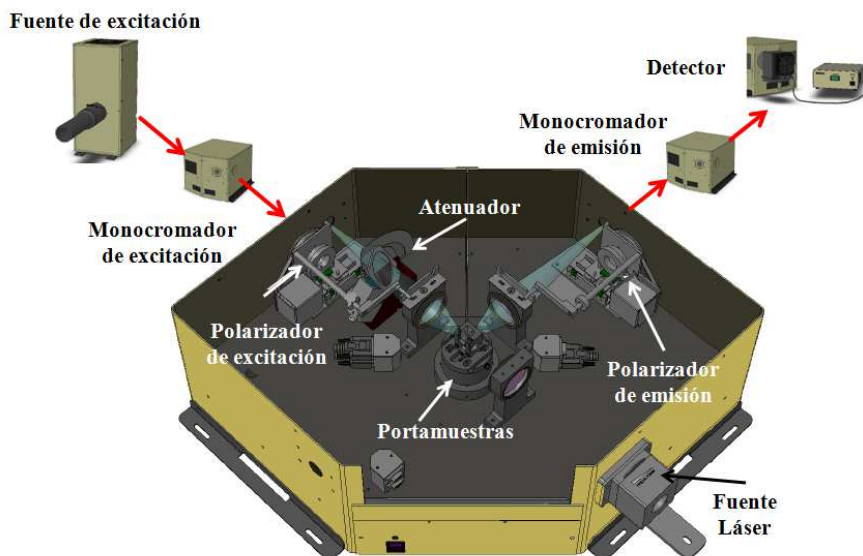


Figura 1. 9. Montaje del Espectrómetro de Fluorescencia.

Para las medidas de películas depositadas sobre sustratos sólidos se utiliza un soporte especialmente diseñado para ello, en el cual el haz de luz proveniente del monocromador de excitación forma un ángulo de 45° con la superficie del sustrato. La orientación del soporte está optimizada para maximizar la cantidad de luz recogida por el detector, la cual abandonará la superficie a un ángulo de 45° . Para el caso de disoluciones, el monocromador de emisión se sitúa formando un ángulo de 90° con respecto a la fuente de radiación, a fin de minimizar la detección de otras radiaciones no provenientes de la propia emisión.

3. Materiales, Reactivos y Tratamientos de Datos

Salvo los compuestos de cianina y quinoleina que fueron sintetizados por J. Sondermann en el Max-Planck-Institute für Biophysikalische Chemie, el resto de materiales y reactivos usados en las experiencias de la presente Memoria fueron adquiridos en las diferentes firmas comerciales que se citan en cada Capítulo. En todas las experiencias el agua es ultrapura, producida en una unidad Millipore Milli-Q tras un pretratamiento en un sistema Millipore de ósmosis inversa ($18\text{M}\Omega\cdot\text{cm}^{-1}$).

Los datos adquiridos de forma digital se han tratado con los programas SigmaPlot,¹² Microcal Origin¹³ y MathCad,¹⁴ que a su vez se han utilizado en la realización de las figuras que se presentan en esta Memoria, y en el caso de MathCad, también en algunas de las simulaciones matemáticas. Asimismo, se ha procedido al tratamiento de imágenes con el paquete Corel, que incluye entre otros Corel Photo Paint o Corel Draw,¹⁵ y el programa Power Point de Office, empleándose además este último en la preparación de los esquemas gráficos que aparecen en los distintos Capítulos.

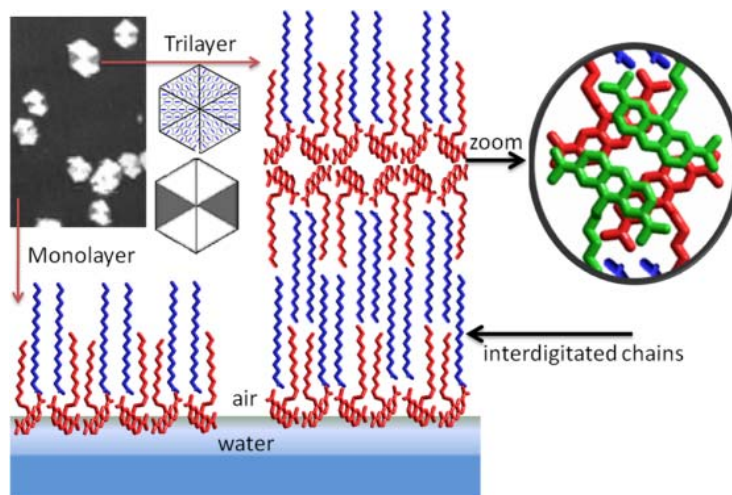
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Resultados y Discusión

Capítulo III

Estudio de Monocapas de Acridina



1. From 2D to 3D at the Air/Water Interface: The Self-Aggregation of the Acridine Dye in Mixed Monolayers

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The formation of well-defined supramolecular structures in the nanoscopic scale is a fundamental step in nanotechnology. The fine control of the layer-by-layer growth of the supramolecular assemblies at interfaces is most desirable. The collapse of a mixed monolayer composed of two surfactants in equimolar ratio: the organic dye N-10-dodecyl acridine (DAO) and stearic acid (SA) is analyzed herein. The collapse process of the DAO/SA mixed monolayer has been monitored using surface pressure-molecular area (π - A), surface potential isotherms, UV-visible reflection spectroscopy, Polarization-Modulated Infrared Reflection-Absorption Spectroscopy (PM-IRRAS), Brewster Angle Microscopy (BAM), and synchrotron-based in situ X-ray Reflectivity (XRR) measurements. The collapse of the DAO/SA mixed monolayer leads to an ordered trilayer. The growth of anisotropic 2D domains of micrometric size is observed during the formation of the trilayer, relating to the ordering of the acridine polar headgroups. The trilayer is organized with the first and third monolayers displaying the polar headgroups pointing to the aqueous subphase, whereas the intermediate layer display the polar headgroups pointing to the air. The trilayer is stabilized by the strong self-aggregation acridine dye group of the DAO molecule. The controlled transition from a monolayer to a trilayer described herein is proposed as a model for further interfacial supramolecular structures of tunable thickness comprising organic dyes.

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1.1. Introduction

The “bottom-up” approach, i. e., the self-assembly of individual building blocks into larger functional structures is fundamental in nanotechnology.¹ In this regard, the controlled transformation of 2D entities into more complex 3D structures at the nanoscale has been highlighted as a suitable alternative for the construction of multifunctional material. The collapse of Langmuir monolayers is of high relevance from a nanotechnological point of view, given that during this process the molecules are self-assembled into 3D supramolecular structures.²⁻³ A computational study on the collapse of Langmuir monolayers of arachidic acid described the atomic interactions leading to the multilayer structure.⁴ In a subsequent study, the influence of divalent calcium cations on the collapse process was thoroughly studied by *in situ* X-ray reflectivity and neutron scattering. This study has been the first experimental proof of the formation of a well-defined trilayer structure formed by a monolayer of arachidic acid at the air/solution interface. This study is also providing interesting insights concerning the formation of 3D crystals at the air/liquid interface.⁵

Moreover, the collapse of a monolayer plays a fundamental role in highly relevant biophysical processes, e. g., pulmonary surfactants in the breathing cycle.⁶⁻⁷ Therefore, the rationale understanding of collapse process of a Langmuir monolayer including a quantitative model is highly desirable. The collapse of a Langmuir monolayer can be described as a phase change in which the Langmuir monolayer is transformed into bulk surfactant under conditions of film compression.⁸

We assume the absence of additional phenomena, e.g., the aggregation of surfactant molecules into soluble aggregates and chemical reactions. In this scenario, the spontaneous compression of a Langmuir monolayer under a constant value of surface pressure is interpreted as the collapse of the Langmuir monolayer.⁹⁻¹⁰

Generally, the term “collapse” has been used to describe a disordering process. However, a number of examples have been reported in the literature

describing the collapse of a Langmuir monolayer spontaneously leading to 3D ordered structures, either bilayers,¹¹⁻¹⁷ trilayers,^{3,12,16,18-27} or multilayers.²⁸⁻³⁴ The study of the process of the collapse of an ordered monolayer is a subject of large interest due to the possibility of controlling the growth of these 3D supramolecular structures by the understanding of the interplay of the involved short- and long-range intermolecular forces

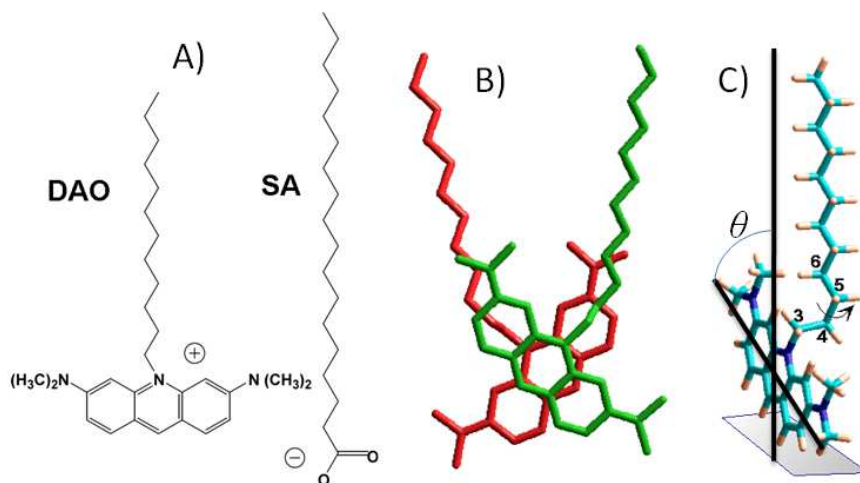


Figure 1.1 A) Molecular structures of N-10-dodecyl acridine (DAO) and stearic acid (SA). B) Model of aggregation of DAO at the air-water interface. C) Rotation of the dihedral plane C(3-6) and tilt angle of the DAO headgroup

Two general mechanisms for the transformation of a Langmuir monolayer into a multilayer have been proposed. In the first mechanism, the Langmuir monolayer folds over itself, leading to a trilayer. In the second mechanism, the trilayer is growing from the monolayer at the boundary of the micrometric domains.^{19,21,24,26,35-37}

The collapse of a mixed monolayer composed of two surfactants in equimolar ratio has been studied herein. The components of the mixed Langmuir monolayer are the organic dye N-10-dodecyl acridine (DAO) and the stearic acid (SA). See Figure 1.1.A for the molecular structures of both components. The mixed Langmuir monolayer DAO/SA has been built by the

cospreeding method, i. e., mixing of both components in the same organic solvent prior to the spreading of the Langmuir monolayer on the air/water interface. A number of in situ experimental techniques for the study of Langmuir monolayers have been used. Surface pressure-molecular area (π - A) and surface potential isotherms provide information on the thermodynamical aspects of the collapse process. UV-visible reflection spectroscopy and Polarization-Modulated Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) offer quantitative information on the polar headgroup and alkyl chain arrangement, respectively. Brewster Angle Microscopy (BAM) allows the direct visualization of the monolayer at the micrometric scale. Synchrotron-based in situ X-ray Reflectivity (XRR) provides the electron density profile of the monolayer.

A previous study in pre-collapse conditions on the mixed Langmuir monolayer DAO/SA showed a quite homogeneous appearance at the mesoscopic size, indicating the formation of a DAO/SA ionic pair.³⁸ In the absence of collapse, two main phenomena are present concerning the polar headgroup of the DAO molecule. First, the spontaneous formation of self-assembled H-aggregates was observed. Second, a change of tilting of the main dipole of the polar headgroup of the DAO molecule was monitored. The spontaneous formation of H-aggregates at the mixed monolayer DAO/SA is driven by the tendency of the DAO headgroups to self-assemble into large aggregates. The DAO molecule in all-trans conformation has a large dipole moment. This large dipole moment results in the intermolecular repulsion between the adjacent DAO molecules in the mixed DAO/SA Langmuir monolayer.³⁹ Given the tendency of DAO to self-assemble into H-aggregates, a partial rotation of the DAO head groups was assumed to compensate this dipolar repulsion, (Figure 1.1B). H-aggregates of a dye occur for the case of a parallel arrangement of the dye units (face-to-face), leading to a blue shift of the absorption band.³⁵ The tilt angle formed between the main axis of the DAO head group and the normal to the air/water interface (θ) ranges from $\theta = 90^\circ$ (low applied surface pressure) to $\theta \approx 55^\circ$ (large applied surface pressure).

From a structural point of view this tilt is caused by the rotation of dihedral angle formed by the atoms C(3)-C(4)-C(5)-C(6) (Figure 1.1C³⁸). The different length of the alkyl chains of the DAO and SA molecules, and the bulkiness of the polar headgroup of the DAO molecule prevent the formation of a highly condensed phase in the monolayer. In other words, the alkyl chains are not oriented fully perpendicular to the interface, adopting an ordered organization, in the DAO/SA mixed monolayer.

In this work, the mesoscopic organization during the collapse of the mixed monolayer DAO/SA has been studied. The ordering within the micrometric domains, as well as the molecular organization of the film is described.

1.2. Experimental Section

Materials. DAO bromide salt and SA were purchased from Fluka and Sigma-Aldrich, respectively, and used as received. Their molecular structures are depicted in Figure 1.1. Chloroform was used as the spreading solvent for dissolving both components. The pure solvent was obtained without purification from Aldrich. Ultrapure water, produced by a Millipore Milli-Q unit, pretreated by a Millipore reverse osmosis system (>18.2 MΩ cm), was used as a subphase. The subphase temperature was 21°C with pH 5.7.

Methods. Surface pressure-molecular area isotherms. Two different models of Nima troughs (NimaTechnology, Coventry, England) were used in this work, both provided with a Wilhelmy-type dynamometric system using a strip of filter paper: a NIMA 611D with one moving barrier for the measurement of the reflection spectra, and a NIMA 601, equipped with two symmetrical barriers to record BAM images. The monolayers were compressed at a speed of ca. 0.1 nm²·min⁻¹·molecule⁻¹. The cospreading method has been used for preparing the mixed monolayer (1:1), mix of the stock solutions of DAO and SA prior to spreading at the air/water interface.

Surface potencial curves: Surface potential at the air/water interface was measured with a surface-potential probe equipped with a vibrating plate

(Kelvin Probe SP1, Accurion Technologies, Göttingen, Germany). Variation of the monolayer surface potential of the monolayer was obtained at the same time as the surface pressure/molecular area isotherm.

UV-vis reflection spectra: UV-vis reflection spectra at normal incidence as the difference in reflectivity (ΔR) of the dye film-covered water surface and the bare surface⁴⁰ were obtained with a Accurion Surface Analysis Spectrometer (RefSpec2 supplied by Accurion GmbH, Goettingen, Germany). All the surface pressure-molecular area isotherms and UV-vis reflections spectra presented herein have been performed at least three times, showing good reproducibility. No dependence of the number of molecules spread on the surface versus mean molecular area was observed for the different experiments.

BAM images: Images of the film morphology were obtained by BAM with a I-Elli2000 (Accurion GmbH), using a Nd:YAG diode laser with wavelength 532 nm and 50 mW, which can be recorded with a lateral resolution of 2 μm . The image processing procedure included a geometrical correction of the image as well as a filtering operation to reduce interference fringes and noise. The microscope and the film balance were located on a table with vibration isolation (anti-vibration system MOD-2 S, Accurion, Goettingen, Germany) in a large class 100 clean room.

PM-IRRAS measurements: PM-IRRAS spectra were recorded using a KSV PMI 550 (KSV NIMA, Espoo, Finland) equipped with an MCT detector. A detailed description of the PM-IRRAS setup and the experimental procedure has already been given elsewhere.⁴¹ The setup consists of an IR source, a Michelson interferometer and an external reflection unit. The infrared radiation intensity was modulated by the interferometer and polarized with a ZnSe polarizer. The beam was then passed through a ZnSe photoelastic modulator, which modulated it between polarization in the plane of incidence (p) and polarization perpendicular to this plane (s) with a fixed frequency of 100 kHz. From the detected intensity (using electronic filtering and demodulation) the two signals, ($R_p - R_s$) and ($R_p + R_s$), were obtained. Only

anisotropic absorption contribute to the PM-IRRAS signal $S \approx (R_p - R_s)/(R_p + R_s)$. Normalized signals were obtained directly by using the following expression: $\Delta S = (S_d - S_o)/S_o$, where S_d and S_o are the signals in the presence and absence of a monolayer, respectively. The angle of incidence of the infrared beam with respect to the surface normal was 80° . Spectra were recorded with a spectral resolution of 8 cm^{-1} and collected using 3000-6000 scans during 5-10 min.

Specular X-Ray Reflectivity (XRR): The specular X-Ray reflectivity (XRR) measurements were performed on the undulator beamline BW1 at HASYLAB, DESY (Hamburg, Germany). XRR provides an averaged electron density profile normal to the interface of all molecules. For reflectivity measurements, the angles of incidence α_i and reflected α_f beams are equal and varied in a range $0.5\alpha_c < \alpha_i (\alpha_f) < 30 \alpha_c$, where $\alpha_c = 0.138$. The reflected intensity was measured by a NaI scintillation detector in the plane of incidence as a function of the vertical scattering vector component Q_z . The electron density profile was obtained from the reflectivity curve using a linear combination of b-splines following the approach of Pedersen and Hamley. The electron density profiles were calculated using the StochFit software.⁴²

1.3. Results and Discussion

1.3.1. Surface pressure – molecular area (π -A) isotherm

Figure 1.2 shows the π -A isotherm of the mixed monolayer DAO/SA, where A represents the average area per molecule (i. e., the DAO and SA molecules are considered equivalent). The onset of the surface pressure is observed at an average area per molecule of ca. 0.8 nm^2 . The starting point of the collapse is observed at a surface pressure of ca. 38 mN/m and an average area per molecule of ca. 0.24 nm^2 . During the collapse process the surface pressure decreases slightly to a fixed value of ca. 37 mN/m while the area decreases simultaneously. A slight increase of the surface pressure is observed at the final point of the collapse process at an average area per molecule of ca. 0.10 nm^2 . A sharp increase in surface pressure is observed for a mean area per

molecule of ca 0.08 nm^2 . Therefore, the collapse of the mixed monolayer DAO/SA from a 2D to a 3D film takes place in the region of the π - A isotherm with a value of average area per molecule ranging from 0.24 to 0.08 nm^2 . Note that the surface pressure is approximately constant along the complete process of collapse. Remarkably, the value of area per molecule at the final point of the collapse (i. e., 0.08 nm^2) is approximately one-third of the initial area (i. e., 0.24 nm^2) therefore suggesting the formation of a trilayer.

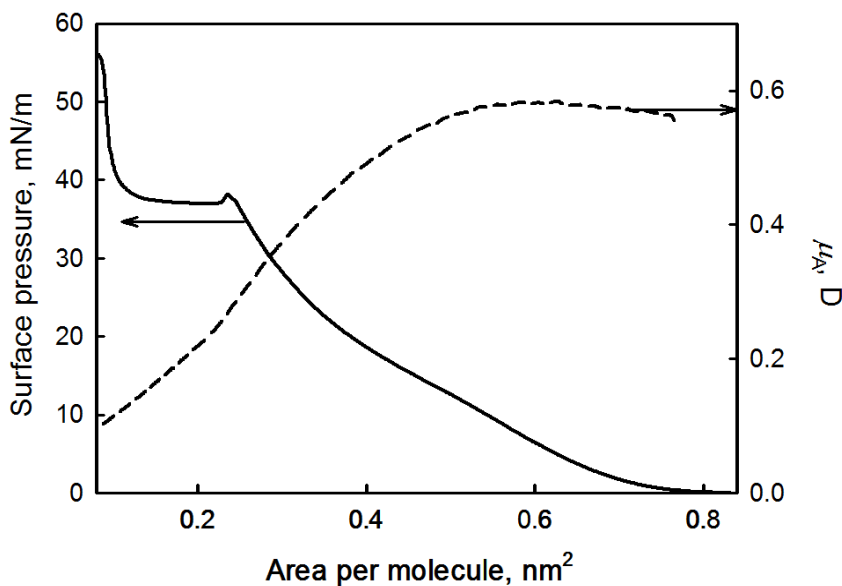


Figure 1.2. Surface pressure - area (π - A , solid line) and apparent dipole moment - area (μ_A - A , dashed line) isotherms of the monolayer DAO/SA.

1.3.2. Surface potential–area isotherm (ΔV - A)

The surface potential of a Langmuir monolayer is dependent on three main factors: a) the dipole moments of the components of the monolayer, b) the relative orientation of the water molecules, and c) the ionic environment and state of the headgroups and subphase. The contribution to the surface potential of the hydrophobic chains is similar for the DAO and SA molecules, given both are saturated linear hydrocarbon chains. Thus, only the contribution of the dipole moments of the headgroups of DAO and SA is

considered as relevant for the observed changes in the surface potential of the mixed monolayer DAO/SA. We adopt herein the general assumption to consider no significant reorientation of the water molecules with the compression of the monolayer. No ions have been added to the pure water subphase. Therefore, the ionic state of the DAO and SA polar headgroups is exclusively considered to have an impact on the ionic environment at the air/water interface. According to the Hemholtz model, the surface potential of a Langmuir monolayer is described by the equation:

$$\Delta V = \frac{\mu_{\perp}}{A \cdot \epsilon_v \cdot \epsilon_0} \quad (1.1)$$

where μ_{\perp} is the total dipole moment of the Langmuir monolayer with a perpendicular orientation to the air/water interface, and ϵ_v and ϵ_0 are the relative dielectric constant at the interface and the permittivity of free space, respectively. The apparent dipole moment, μ_A , is defined as:

$$\mu_A = \Delta V \cdot A \cdot \epsilon_0 = \frac{\mu_{\perp}}{\epsilon_v} \quad (1.2)$$

The plot $\mu_A - A$ is shown in Figure 1.2 as adashed line. For $A > 0.5 \text{ nm}^2$, μ_A is ca. 0.58 D. When the area decreases, μ_A decreases, reaching before the collapse a value of μ_A of ca. 0.25 D ($A = 0.24 \text{ nm}^2$). This decrease was related to the partial rotation of the acridine group (i. e., the polar headgroup of the DAO molecule). The alkyl chains of the DAO molecule are arranged in all-trans conformation, resulting in a large dipole moment of the whole molecule. The dipole moment of the hydrophobic chains in a compressed Langmuir monolayer has been appointed as the main contribution to the surface potential in several examples (e. g., a Langmuir monolayer of pure stearic acid). In that case, the contribution of the alkyl chains was assumed as ca. 230 mV in an overall value of 300 mV, with a minor negative contribution from the water layer underneath the monolayer. This last contribution might change as a function of the degree of ionization. In the case of the DAO

molecule, the polar headgroup also bears one charge per molecule. Despite the DAO headgroup is bulkier than the SA headgroup, we assumed a similar relative contribution to the overall surface potential of the mixed monolayer. Moreover, the charges of DAO and SA are of opposite sign. The cancellation of the contribution of the polar headgroups to the surface potential of the mixed monolayer is therefore expected.³⁶

This large dipole moment leads to a significant repulsion between adjacent DAO molecules. The DAO headgroups within the mixed DAO/SA monolayers have a certain degree of mobility. In other words, the DAO headgroups might change the relative orientation of the main axis of the DAO group (i. e., the axis connecting the amine groups, to reduce the intermolecular repulsion). Therefore, the DAO headgroups from neighboring DAO molecules within the mixed monolayer can rotate in opposite directions.³⁸ This rotation effectively reduces the intermolecular repulsion between the individual dipole moments of the DAO headgroups, (Figure 1.1B). The reduction of this intermolecular repulsion leads to a reduction in the overall value of μ_A of the mixed monolayer DAO/SA.

For $A < 0.24 \text{ nm}^2$, μ_A decreases linearly with decreasing area with a slope approximately equal to unity. Thus, for A ca. 0.08 nm^2 , μ_A is approximately one third of the value at the beginning of the collapse (i. e., 0.09 D). This sharp decline of the dipole moment per molecule can exclusively be explained by the formation of a trilayer at the air/water interface. The top bilayer should have the two monolayers with opposite orientation, resulting in the cancelation of their contribution to the apparent dipole moment of the whole trilayer.

1.3.3. Brewster Angle Microscopy (BAM)

The Brewster Angle Microscopy (BAM) allows for the in situ imaging of the mixed monolayer DAO/SA at the air/water interface. The BAM can resolve the formation of domains with micrometer resolution. Figure 1.3 shows representative BAM images of the mixed monolayer DAO/SA. As previously mentioned, for $A \geq 0.24 \text{ nm}^2$, the mixed monolayer DAO/SA appear homogeneous in the BAM images, with no apparent formation of domains. The homogeneity of the mixed monolayer DAO/SA has been related to the complete miscibility of the components. On the contrary, for $A \leq 0.24 \text{ nm}^2$, the formation of hexagonal domains is observed, see Fig. 1.3B,C. These domains increase in size with the decrease in area, eventually deforming as shown in Figure 1.3D.

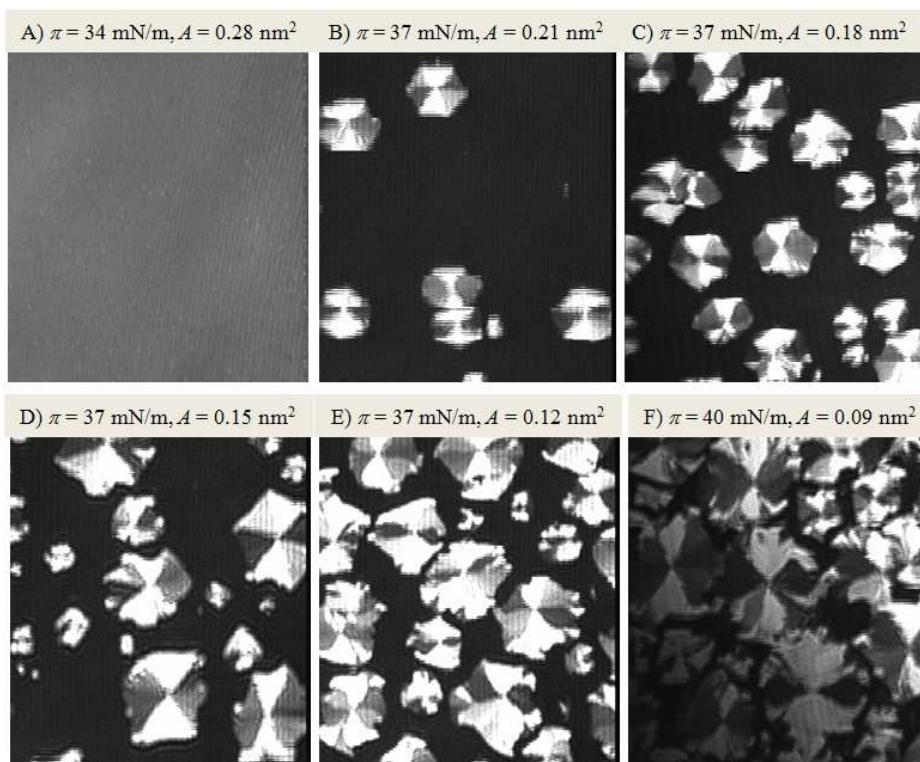


Figure 1.3. BAM images of the mixed monolayer DAO/SA. (A) Region preceding collapse region. (B-F) Collapse region. The width of each frame is $215 \mu\text{m}$.

Remarkably, the hexagonal domains display internal anisotropy, i.e., there are bright and dark regions inside the domain. The anisotropy in the orientation of dye headgroups led to inner textures within the domains in related cases, as previously studied by our group.⁴³⁻⁴⁴ Note that the dark regions of the domains are always brighter than the surrounding. The dark areas of the domains are extended horizontally, (i.e. perpendicular to the incidence direction of the laser used in the BAM experiments). The existence of anisotropy inside the domains indicates the existence of distinct molecular ordering of the acridine dye moiety for the different regions within the domain, due to the enhancement of reflected radiation by certain absorption of the incoming radiation during the BAM experiment. Similar results have been reported during BAM experiments concerning the organization of the alkyl chains from Vollhardt et al.

In such cases, either the different azimuthal angle of the alkyl chains of the lipids within the domains⁴⁵⁻⁴⁶ or the effect of a chiral center of the surfactant, led to different inner textures always related to the organization of the alkyl chains.⁴⁷⁻⁴⁸ However, in the case described herein, the anisotropy in the BAM images is caused by the different absorption of the dye headgroups.⁴⁴

1.3.4. UV-vis reflection spectra

The UV-vis reflection spectroscopy at the air/water interface offers in situ quantitative information on the presence and orientation of the chromophores at the air/water interface. The UV-vis reflection spectroscopy is exclusively sensitive to the molecules existing at the air/water interface, thus discarding any signal from the subphase. For a Langmuir monolayer containing UV-vis absorbing molecules, the reflection of an incident light at the interface is enhanced by⁴⁹

$$\Delta R = R_{D,S} - R_S = 2.303 \times 10^3 \cdot f_o \cdot \epsilon \cdot \sqrt{R_S} \cdot \Gamma \quad (1.3)$$

where $R_S = 0.02$ and $R_{D,S}$ are the reflectivity of the interface without and with

the presence of the Langmuir monolayer, respectively, ε is the molar absorption coefficient in $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$ units, Γ is the surface concentration of the monolayer, in $\text{mol} \cdot \text{cm}^{-2}$ units, and f_0 is the orientation factor. In equation (1.3), ε coefficient is obtained from bulk measurements (i.e., DAO solution); therefore no preferred orientation is included. However, anisotropy in the orientation of the dipoles is expected at the air/water interface. Assuming a homogeneous orientation of all molecules at the interface, the orientation factor, f_0 , accounts for the change in the absorption properties of the chromophore due to anisotropy. Given a nondegenerate absorption band, that is, with only one component of the transition dipole, the orientation factor is⁵⁰

$$f_0 = \frac{3}{2} \langle \sin^2(\theta) \rangle \quad (1.4)$$

where θ is the angle formed between the transition dipole and the z axis (i.e., the normal axis to the air/water interface). The brackets indicate a mean value. UV-vis reflection spectra are often expressed in normalized units in order to discard any additional effect to the variation of the surface concentration of the chromophore units at the interface. The surface concentration of the dye, the DAO molecule, is expressed by

$$\Gamma = \frac{10^{14}}{N_A A_{DAO}} \quad (1.5)$$

where N_A is the Avogadro number, and A_{DAO} is the molecular area of DAO. A_{DAO} is obtained from the π -A isotherms by $A_{DAO} = A/X_{DAO}$, where $X_{DAO} = 0.5$ is the molar ratio of the DAO component. The normalized reflection signal ΔR_{norm} is the product of the absolute reflection signal and the molecular area of the chromophore:

$$\Delta R_{\text{norm}} = A_{DAO} \times \Delta R = \frac{2.303 \times 10^{17} f_0 \varepsilon}{N_A} \sqrt{R_s} = 5.41 \times 10^{-8} f_0 \varepsilon \quad (1.6)$$

ΔR_{norm} has $\text{nm}^2 \cdot \text{molecule}^{-1}$ units. The normalized reflection spectra offer information on molecular aggregation, as well as molecular orientation.

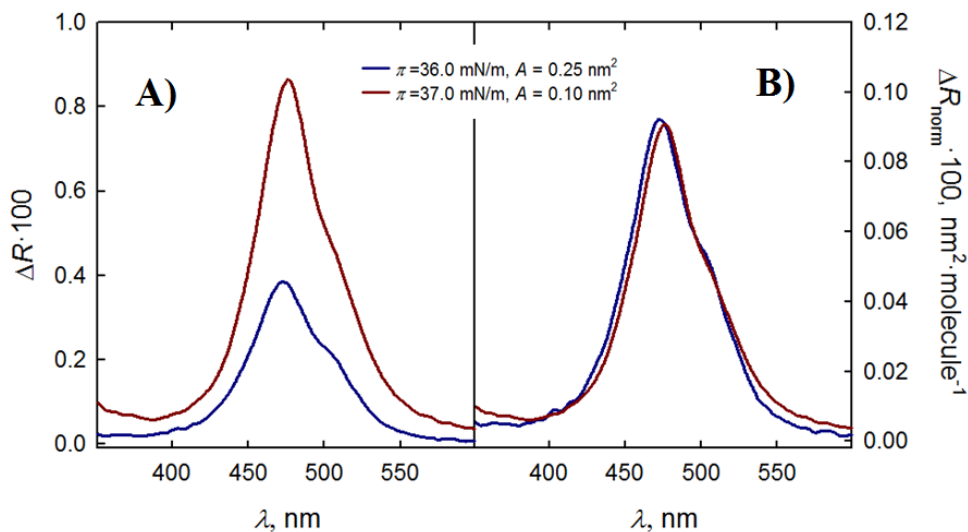


Figure 1.4. A) UV-vis reflection spectra (ΔR) for the DAO/SA = 1:1 mixed monolayer. B) Normalized reflection spectra ($\Delta R_{\text{norm}} = \Delta R \cdot A_{\text{DAO}}$). The values of total area per molecule, A , are noted in the Figure.

Figure 1.4A shows representative UV-vis reflection spectra corresponding to different values of molecular area, both before and during the collapse of the DAO/SA mixed monolayer. After the collapse of the mixed monolayer has taken place, the absolute value of the UV-vis reflection is increased approximately 3-fold with respect to the value before the collapse. This increase of the UV-vis reflection signal is related to an increase in the surface concentration of the DAO molecule at the air/water interface, equations 1.3 and 1.5.

The normalized UV-vis reflection spectra, ΔR_{norm} , are shown in Figure 1.4B. The spectra obtained immediately before the collapse (blue) and at the end of the collapse (red) are nearly coincident, therefore confirming that the previously described increase of the UV-vis reflection signal is due to an

increase of the surface concentration of DAO molecules and not to a reorientation of the chromophore groups.

The value of the normalized UV-vis reflection spectra, ΔR_{norm} , displays almost no change with the collapse process. On the contrary, the apparent dipole moment per molecule, μ_A , diminishes to one third of the initial value with the collapse. The different trends of these two physical properties per molecule seem contradictory. The explanation for this difference is as follows: the apparent dipole moment per molecule decreases due to two-thirds of the total molecules are in the top bilayer with opposite orientation; therefore their contribution to the surface potential is cancelled. On the other hand, the normalized UV-vis reflection spectra, ΔR_{norm} , are exclusively depending on the squared transition dipole. Therefore, the global value of reflection intensity is not depending on the orientation of the chromophore groups. In the case of the top bilayer, the chromophore groups have opposite orientations, that do not affect value of the reflection signal.

These data reinforce the hypothesis of the formation of a trilayer at the air/water interface, where a bilayer is positioned on the monolayer in direct contact with the aqueous phase, as shown schematically in Figure 1.5. This molecular arrangement agrees with the observed experimental data from the two commented techniques. First, the dipole moments of the top bilayer are cancelled against each monolayer leaflet. Second, the UV-vis reflection signal is increased by 3-fold. The observed three-fold increase in the absolute value of the reflection signal corresponds to an increase of the number of absorbing molecules on the probed area by a factor of three. Given that the surface pressure is almost constant during this increase, and that the UV-vis reflection signal exclusively arises from the chromophores at the air/water interface, we assume that there is a multilayer formation, in this case a trilayer.

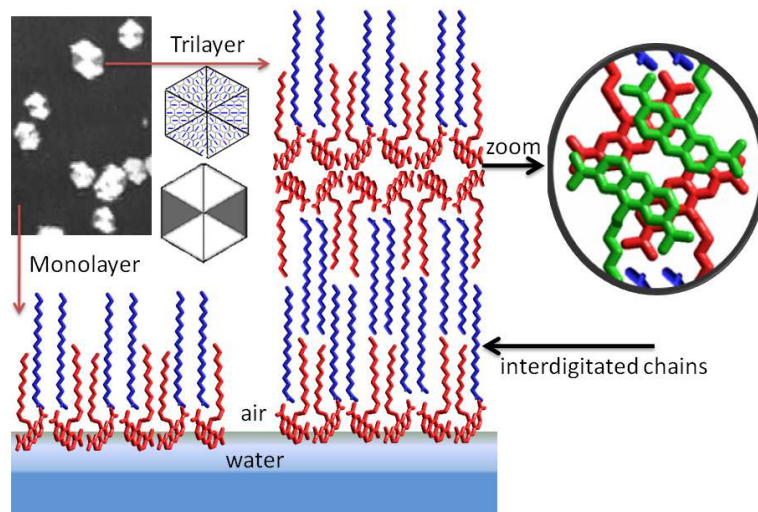


Figure 1.5. Schematic model of the trilayer structure formed during the collapse process. DAO molecules are red (or green when are superimposed), and SA molecules are blue.

1.3.5. Synchrotron-based in situ X-ray Reflectivity (XRR).

XRR experiments allow the in situ determination of the vertical electron density profile of soft matter thin films.^{51,52} Figure 1.6 shows the reflectivity data of the DAO/SA mixed monolayer monolayer before the collapse (Figure. 1.6A, $\pi = 34$ mN/m, $A = 0.28$ nm², and after the collapse, Fig. 1.6B, $\pi = 37$ mN/m, $A = 0.10$ nm²).

Before the collapse, the reflectivity data have been fitted to a two-box model with the fitting parameters shown in Table 1.1. The continuous line in Figure 1.6A shows the reflectivity using those mentioned parameters.

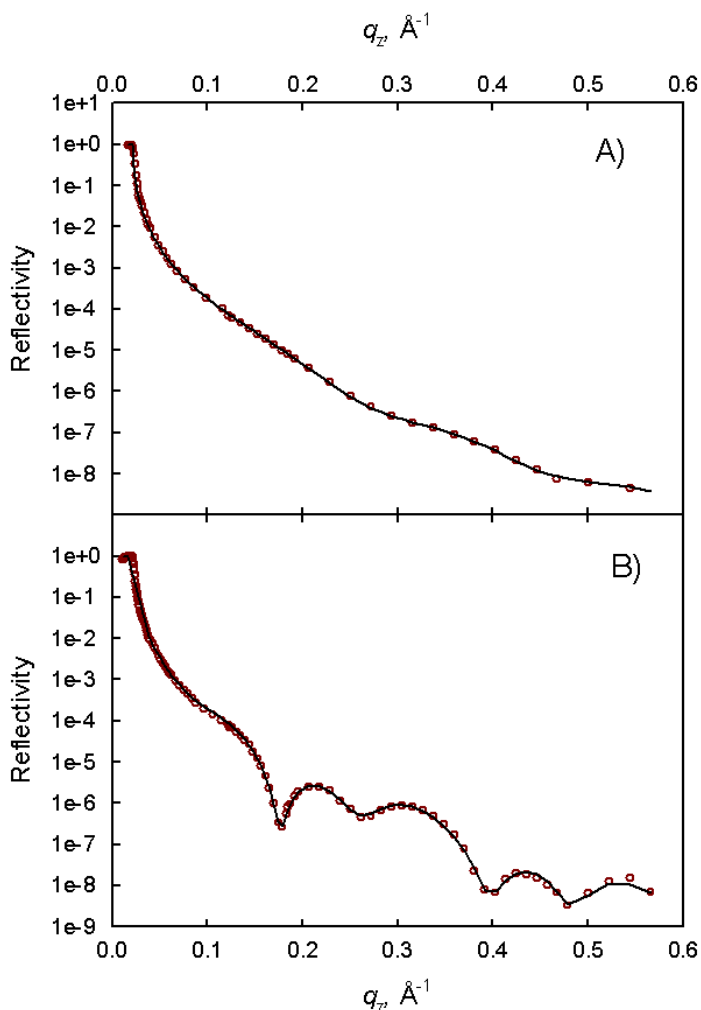


Figure 1.6. A) Red circles: X-ray reflectivity for the DOA:SA mixed monolayer at $\pi = 34$ mN/m and $A = 0.28$ nm². Black line: numerical fit using two-box model. The fitting parameters are shown in Table 1.1. B) Red circles: X-ray reflectivity for DOA:SA mixed monolayer at $\pi = 37$ mN/m and $A = 0.10$ nm². Black line: numerical fit using five-box model. The fitting parameters are shown in Table 1.2.

The vertical profile of relative electron density (ρ/ρ_{water}) to the air/water interface plane was determined from the spatial distribution of different atoms using simulations with HyperChem.⁵³ An all-trans configuration of the alkyl chains and a tilting angle of the acridine group of 55° , according to the previously deduced value, have been assumed.³⁶

Table 1.1. Numerical fit of the reflectivity data obtained at $\pi = 30$ mN/m and $A = 0.28$ nm².

Two- box model			Theoretical three- box model		
	one box	two boxes	one box	two boxes	three boxes
ρ/ρ_{water}	0.82 ± 0.07	1.12 ± 0.09	0.4	0.8	1.35
Length / nm	0.81 ± 0.01	1.72 ± 0.01	1.13	0.92	0.96
$\sigma / \text{\AA}$	3.19 ± 0.03	--	--		
Total Length	2.532 nm	--	3.01 nm		

Left: parameter obtained from the two-box model. **Right:** Parameters obtained in the theoretical model develop in Figure 1.7. σ , interfacial roughness.

Figure 1.7 shows the detailed results of electron density. The relative contributions of the electron densities of the DAO and SA molecules to the total signal are shown as red and blue dashed lines, respectively. The electron density corresponding to the water subphase is modelled as a Gaussian distribution for the contact region with the polar group and plot as the dashed black line. The overall relative electron density is represented as a solid green line.

A theoretical model using three boxes can be used for simulate the electron density profile based on the molecular arrangement obtained by HyperChem. This is a simple model (e. g., not including the hydrodynamic waves of the air/liquid interface). The polar headgroups of both DAO and SA occupy the closest box to the water, being noted as box 3. The alkyl chains are included in the box 2. Because of the shorter length of the alkyl chain of the DAO molecule when compared to the SA molecule, a segment of the alkyl chains of the SA molecules is included in box 1. Using this theoretical model

the mixed monolayer DAO/SA is assumed to be composed of three boxes, (Figure 1.7). Note that the experimental data are fitted using a model including two boxes. The fitting parameters for both the theoretical model of three boxes and the model for fitting the experimental results of two boxes are shown in Figure 1.7 and Table 1.1.

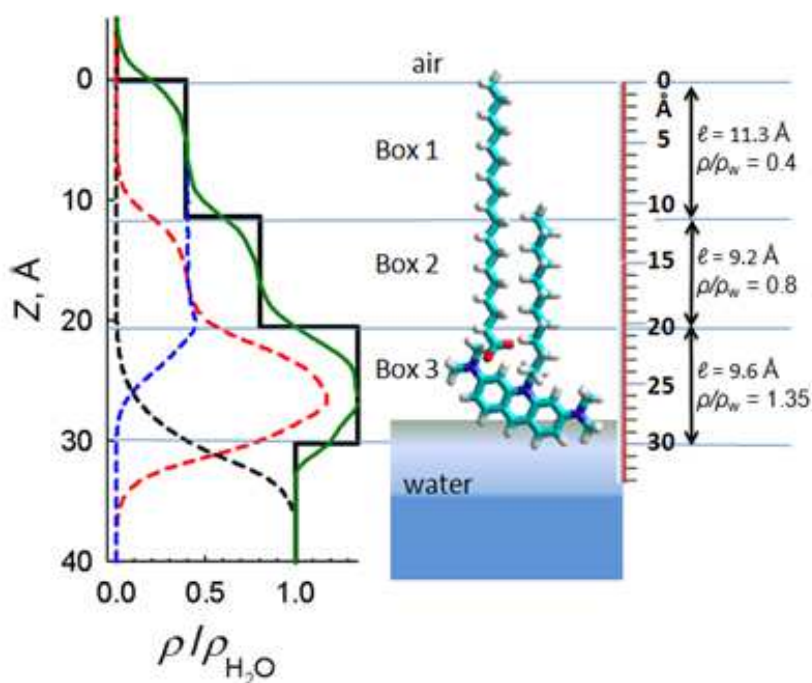


Figure 1.7. Left: Theoretical vertical profile of the relative electron density for DAO (dashed red line), SA (dashed blue line), water (dashed black line) and overall (solid green line). The solid black line represents the three box theoretical model. Right: Vertical spatial distribution of DAO and SA.

Using a three-box model to fit the experimental data requires a large number of numerical parameters into the model, allowing good fits for different collections of numerical parameters. However, there are significant similarities between the fitting parameters obtained by adjusting the reflectivity with a 2-box and the theoretical model. First, the thickness of the second box in the adjustment, 1.723 nm, is quite close to the sum of the thicknesses of the boxes 2 and 3 of the theoretical model, 1.88 nm. The

relative electron density of this second box is $\rho/\rho_{\text{water}} = 1.12$, almost exactly the arithmetic mean value of those electron densities obtained in the theoretical model, $\rho/\rho_{\text{water}} = 0.8$ and 1.35 . On the other hand, some discrepancies are found in the parameters of the first box. Note that the alkyl chains have been assumed to adopt an all-trans configuration, which does not correspond to the experimental situation. A certain tilting of the alkyl chains with respect to the air/water interface plane is expected. The tilting of the alkyl chains leads to a reduction of the observed thickness by X-ray reflectivity as well as a slight increase in the electronic density value. Both trends are observed in the parameters used for the fitting of the X-ray reflectivity data. Note that the total thickness of the films is in both cases within the same order of magnitude, 2.5 nm for the two-box model, compared to 3.0 nm for the theoretical model.

The reflectivity data for the DAO/SA mixed monolayer upon the finalization of the collapse process, shown in Figure 1.6B as red circles, have been fitted using a five-box model. In this case a theoretical model has been used based on the existence of a trilayer of DAO/SA at the air/water interface, as depicted in Figure 1.5 and Figure 1.8. The electron density of the mixed monolayer DAO/SA is shown as a green line in Figure 1.8. In the trilayer model, the alkyl chains of the DAO and SA molecules are interdigitated to a certain extent. The interdigitation is defined herein as the overlapping of the alkyl chains of two different monolayers on the z-axis. The different lengths of the alkyl chains of the DAO and SA molecules favors the interdigitation, allowing the attractive interactions between the alkyl chains of both monolayers. The interdigitation of the alkyl chains leads to a supramolecular network with no free space between the three monolayers, contributing to the stability of the trilayer. An all-trans configuration and a perpendicular orientation to the air/water interface of the alkyl chains are assumed. The total thickness of the trilayer is therefore ca. 8.7 nm. The thickness and the relative densities of each box are shown in Figure 1.8 and Table 1.2 (right).

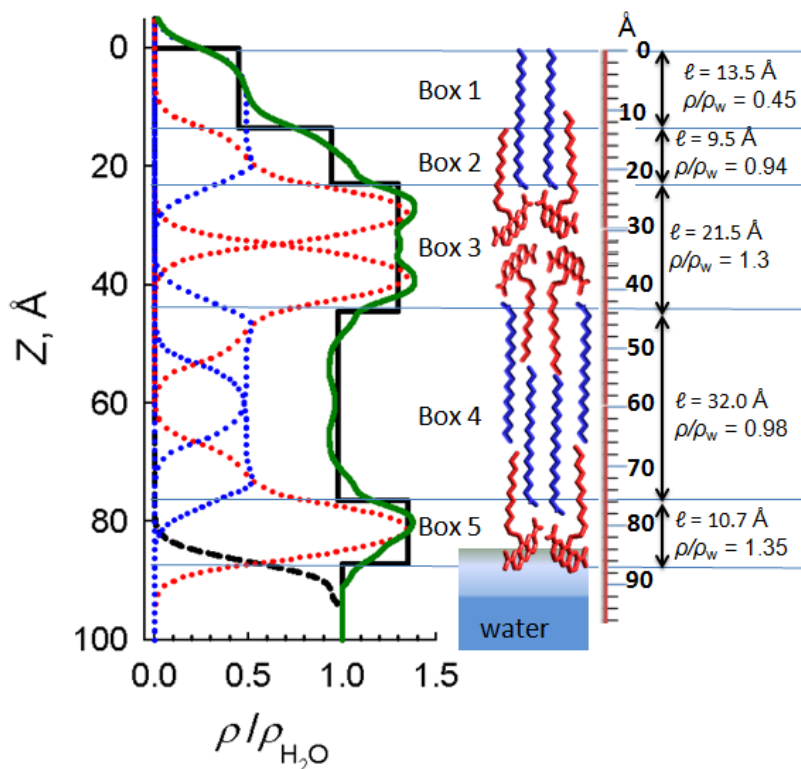


Figure 1.8. Left: Theoretical vertical profile of the relative electron density for DAO (dashed red line), SA (blue dashed line), water (dashed black line) and overall (solid green line). The solid black line represent the five box theoretical model. Right: Vertical spatial distribution of DAO and SA. DAO molecules are red, and SA molecules are blue .

Figure 1.6B shows the experimental data and the numerical fitting of the reflectivity data for the DAO/SA trilayer (red circles and black line, respectively). The fitting parameters are shown in Table 1.2 (left). A certain discrepancy between the fitting parameters and the theoretical model is observed. The most relevant difference concerns the fitting parameters of the boxes 2 and 3. Comparing the fit parameters with the theoretical model (Table 1.2), shows that the values of thickness and electron density of box 2 increase by decreasing the parameters of the box 3, maintaining approximate constant values of the thickness and average electron density. This variation in the fitting parameters of the box 2 can be related to a separation between the boxes 2 and 3, rather rougher than that shown in Figure 1.8 (theoretical

model). The total thickness of the trilayer obtained from the fitting of the reflectivity data is 7.57 nm. The thickness of the trilayer according to the previously described theoretical model is 8.72 nm. This discrepancy can be attributed to two reasons: the alkyl chains in the trilayer are not completely perpendicular to the air/water interface, and the inhomogeneity of the monolayer results in a certain coexistence of monolayer and trilayer at the air/water interface, even for $\pi = 37$ mN/m, $A = 0.10$ nm², (Figure 1.3).

Table 2. Numerical fit of the reflectivity data obtained at $\pi = 36.8$ mN/m and $A = 0.10$ nm²

	5 box model					Theoretical model				
	Box 1	Box 2	Box 3	Box 4	Box 5	Box 1	Box 2	Box 3	Box 4	Box 5
ρ/ρ_{water}	0.36 ± 0.082	1.0 ± 0.13	1.3 ± 0.1	0.97 ± 0.08	1.2 ± 0.2	0.45	0.94	1.3	0.98	1.35
Length / nm	0.83 ± 0.01	1.73 ± 0.01	1.25 ± 0.01	2.71 ± 0.01	1.05 ± 0.01	1.35	0.95	2.15	3.2	1.07
$\sigma / \text{Å}$	2.94 ± 0.05									
Total Length	7.584 nm					8.72 nm				

In spite of the discrepancies found between the experimental electronic density data and those calculated for an ideal trilayer of DAO/SA, the reflectivity data confirm the formation of the three-layer by obtaining thicknesses corresponding to approximately three times those obtained for the monolayer. It is noteworthy that the reflectivity data confirm the existence of a region (box 3) in which there is an increase of the electron density with respect to adjacent boxes (box 2 and 4), which can be exclusively explained if

the formation of a trilayer takes place with structure similar to that proposed in Figures 1.5 and 1.8.

The dense packing of the alkyl chains suggests the ordering of those chains into a crystalline structure, which should lead to a significant signal in Grazing Incidence X-ray Diffraction (GIXD).⁵⁴ Indeed, we also expected a clear GIXD signal. However, there was no GIXD signal obtained during the synchrotron experiments in any case, either before or after the collapse. The experiments were repeated at a different beam time in order to check the reproducibility, and similar results were obtained.

1.3.6. PM-IRRAS measurements

Figure 1.9 shows the PM-IRRAS spectrum in the 2700-3800 cm^{-1} region of the DOA/SA mixed monolayer. Prior to collapse ($\pi = 20$ mN/m and 30 mN/m), the asymmetric and symmetric stretching mode of methylene, $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$, are barely distinguishable. This fact indicates that the alkyl chains are not oriented vertically to the interface and should not be in a crystalline state. Note also that for $\pi = 20$ mN/m, $A \approx 0.4$ nm^2 , whereas for $\pi = 30$ mN/m, $A \approx 0.3$ nm^2 per alkyl chain. Furthermore, as commented previously, the lengths of the alkyl chains of DAO and SA molecules differ.

On the contrary, after the collapse, especially when the collapse is completed ($\pi = 40$ mN/m, $A = 0.09$ nm^2), the $\nu_{\text{as}}(\text{CH}_2)$ mode at 2919 cm^{-1} and $\nu_{\text{s}}(\text{CH}_2)$ mode at 2849 cm^{-1} are clearly distinguishable. Previous IR studies have shown that the locations of $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ modes are sensitive indicators for the lateral interactions between alkyl chains.⁵⁵⁻⁵⁹ Thus, the band position for the $\nu_{\text{as}}(\text{CH}_2)$ mode is 8 cm^{-1} lower in the crystalline state (2920 cm^{-1}) than that for the liquid state (2928 cm^{-1}). whereas for the $\nu_{\text{s}}(\text{CH}_2)$ mode the band position is 6 cm^{-1} lower in the crystalline sample (2850 cm^{-1}) than in the liquid (2856 cm^{-1}).^{59,60} The low wavenumbers observed for the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ modes are indicative of tightly packing of the hydrocarbon chains of both DAO and SA at the end of collapse, (Figure 1.9)

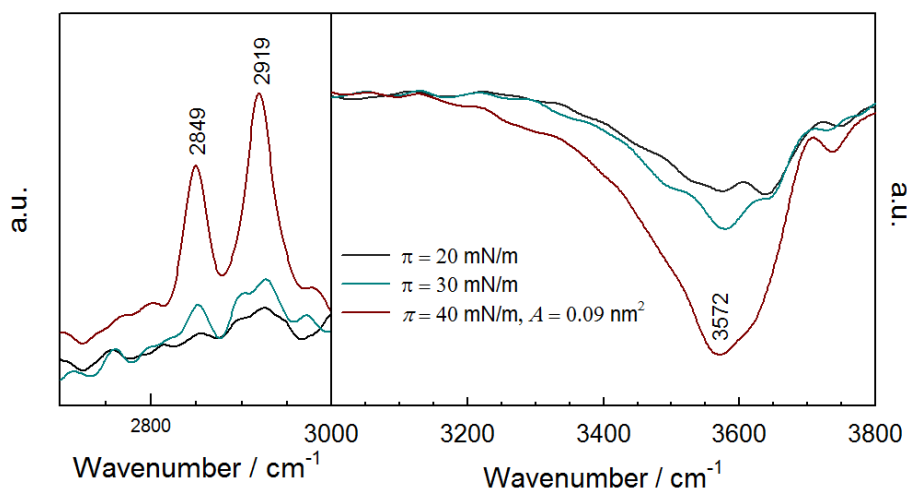


Figure 1.9. PM-IRRAS spectrum (2700-3800 cm⁻¹ region) of the DOA:SA mixed monolayer at different values of surface pressure.

Likewise, the bandwidth (i.e, fwhm full width at half-maximum) of $\nu_{as}(\text{CH}_2)$ mode has been used to provide a measure of adlayer order.⁵⁹⁻⁶¹ Whereas those bands for the crystalline state are narrower ($\leq 20\text{cm}^{-1}$), bandwidths for the disordered liquid state are very broad ($\geq 28\text{cm}^{-1}$). In this case, the fwhm of $\nu_{as}(\text{CH}_2)$ band reaches a value of 32cm^{-1} when the collapse is completed ($\pi = 40\text{ mN/m}$, $A = 0.09\text{ nm}^2$).

This value of fwhm indicates that the alkyl chains are rather disordered in the liquid state. This experimental observation is in apparent contradiction to the solid state of the alkyl chains as described observe by the values of the maximum wavenumber of the PM-IRRAS bands as well by the BAM and X-ray reflectivity. This apparent contradiction is related to the two different environments of the alkyl chains in the trilayer. In the first environment, the alkyls chains of the two monolayers closest to the aqueous subphase are interdigitated (Figure 1.5). Therefore a highly packed, quasi-crystalline state is expected. In the second environment, the alkyl chains of the outermost monolayer are in a disordered quasi-liquid state. The latter scenario represents approximately one-third of the total number of alkyl chains. The

position of the $\nu_{as}(\text{CH}_2)$ mode at 2919 cm^{-1} indicates the quasi-crystalline state of the interdigitated alkyl chains, and the bandwidths indicate the state of disordered chains outer monolayer.

At 3572 cm^{-1} there is a negative band that arises from the OH stretch of water (Figure 1.9). The water O-H stretching vibration present in the reference signal is reduced in the reflectivity signal from the monolayer-covered surface because the surfactant layer replaces a water layer and masks partially the OH stretching vibration.³⁷ The result is a strong negative band that is related to the effective thickness of the monolayer. The increase in the intensity of this band when passing from the previous to the posterior collapse region should be related to the increased thickness of the material at the air/water interface and therefore to the trilayer formation.

1.4. Conclusion

The collapse process of the DAO/SA mixed Langmuir monolayer has been analyzed by a number of in situ experimental techniques at the air/water interface. The experimental results have demonstrated the formation of an ordered trilayer as a result of the collapse. X-ray reflectivity measurements showed a value of thickness of the trilayer, as being ca. 7.6 nm. This value of thickness of the trilayer is 3 times the value of thickness for the monolayer, ca. 2.5 nm.

In the proposed trilayer model, the first and third monolayers orient their polar groups toward the aqueous subphase, and the intermediate layer has an inverted orientation in order to promote interactions between polar groups and between alkyl chains. This molecular arrangement is particularly favored by the strong tendency to self-aggregation of the DAO polar headgroup and by the different lengths of the alkyl chains of DAO and SA molecules. The interdigitation of the alkyl chains from DAO and SA molecule takes place as observed by PM-IRRAS, detecting a strong increase of the methylene (CH_2) IR signals during trilayer formation, being related to vertical orientation and quasi-crystalline order of these imbricate alkyl chains.

A striking growth of hexagonal domains with internal anisotropy is observed by BAM during trilayer formation. The anisotropy has been related to the existence of order due to the acridine polar groups (i.e. both in acridine the monolayer in contact with the aqueous subphase), as in the two additional monolayers.

The in situ visualization of the molecular aggregates formed by the acridine group is feasible because of the absorption of radiation from the aggregates at the wavelength used in the laser used in BAM experiments. Similar hexagonal domains with internal anisotropy have been observed in the mixed monolayers of dimyristoyl-phosphatidic acid (DMPA) and methylene blue (MB).⁴³ However, in that case the domains are formed during the compression of the monolayer, whereas herein the domains are formed and grow during the collapse process. The same physical phenomenon is responsible for the inner textures inside the domains in both cases. The dark and bright regions of domains can be related to different orientations of the transition dipoles projections of the acridine group on the air/water interface.

The strong tendency of the acridine group in the DAO polar headgroup to self-aggregation is the main driving force leading to the formation of a trilayer. The interdigitation of the alkyl chains of DAO and SA molecules contributes significantly to the stability of the 3D structure of the trilayer, observed as hexagonal domains.

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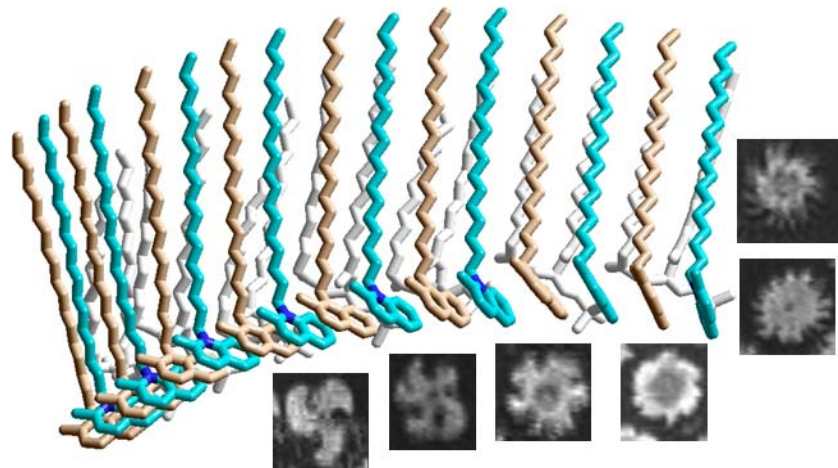
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Resultados y Discusión

Capítulo IV

Estudio de Monocapas de Cianina y derivados



1.2D Chiral Structures in Quinoline Mixed Langmuir Monolayers

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Chirality at interfaces is a relevant topic in nanoscience, as well as a key point for prebiotic chemistry. Mixed Langmuir monolayers, composed of the anionic phospholipid dimyristoyl phosphatidic acid (DMPA) and the cationic amphiphilic quinoline derivative 2-methyl-1-octadecylquinoline (MQ) have been built at the air-water interface. Both DMPA and MQ molecules are miscible, thus the equimolar mixture yields homogeneous monolayers completely. Chiral domains have been formed by this monolayer, and observed in situ by Brewster Angle Microscopy (BAM). These chiral domains display a large array of shapes and sizes. The chirality of the monolayers has been confirmed by circular dichroism spectroscopy. The ordered aggregation of the quinoline group into large chiral supramolecular structures is proposed as the molecular origin of the observed chirality. Theoretical simulations using molecular mechanics confirm the strong trend of the quinoline group to form chiral aggregates. The great diversity in the size and shape of the chiral domains has been found to be strongly influenced by the competition between two nuclei growth mechanisms. An experimental procedure allowing a minimized growth through one of these mechanism is proposed, achieving a homogeneous distribution of ring-shaped domains. An overshoot in the π - A isotherms of this mixed monolayer appears at an intermediate surface pressure. This overshoot is interpreted as being due to the large difference between the surface pressure which starts the nuclei formation, π_{crit} , and the superficial pressure which the nuclei can grow, π_e . The rather small π_e value compared to π_{crit} observed for this system must be attributed to the molecular interactions involved in the mixed monolayer, which facilitate the incorporation of molecules in preformed nuclei.

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1.1. Introduction

The air-water interface is an exceptional system where the 2D confinement of amphiphilic molecules imposes geometric constraints for the formed molecular aggregates.¹ The 2D confinement can induce the chirality of prochiral molecules, i. e., molecules whose structure cannot be superimposed by a simple in-plane rotation.² The interfacial confinement of prebiotic molecules at air-water interfaces might have provided the conditions for the appearance of the first chiral biomolecular entities.³

The supramolecular chirality is the result of a suitable adjacent molecule packaging as result of its aggregation, that is, the bottom-up approximation.⁴ In this way, some achiral molecules could form chiral assemblies at the air-water interface.⁵⁻¹² Additionally, the chirality can be mechanically induced¹³⁻¹⁸ or induced and amplified on surfaces.¹⁹⁻²⁴

2D supramolecular chiral structures at the air-liquid interface can be assessed in situ by Brewster Angle Microscopy (BAM).^{17,25-30} The control of the size, shape, and periodicity of the domains formed at the interface is of great interest because the mesoscopic structured surfaces may serve as a platform in engineering the biological/material interface and in constructing biofunctionalized structures and programmed systems.³¹⁻³²

In previous studies we analyzed the mixed monolayers formed by the anionic phospholipid dimyristoyl phosphatidic acid (DMPA), and a cationic amphiphilic derivative of the hemicyanine dye (HSP), using a molar ratio 1:1.²⁹⁻³⁰ The HSP:DMPA mixed monolayer was stabilized at the air-water interface by the electrostatic interactions between the polar headgroups and the hydrophobic interactions between the alkyl chains of HSP and DMPA molecules. Given the shorter length of the alkyl chains of the DMPA molecule compared to the HSP molecule, the HSP headgroup has a large freedom to adopt different conformations, being able to display a long-range chiral aggregation. HSP is a prochiral molecule which might display chirality when confined in a 2D medium.² However, in this case, the chirality is not caused by a spontaneous breaking of symmetry, because only one of the chiral

aggregates can be observed.²⁹⁻³⁰ On the contrary, the chirality is induced by the presence of a chiral group in the DMPA. The L optical isomer of DMPA was used because this optical isomer is the only one commercially available.

As a continuation of previous studies,²⁹⁻³⁰ herein we study the equimolar mixed monolayers of DMPA and the cationic 2-methyl-1-octadecylquinoline (MQ, see Figure 1.1 for structures). In our previous work, we have focused on the effect of varying the ratio of surface area between the components in mixed Langmuir monolayers. On the other hand, herein we use a different point of view, thus studying the impact of using a significantly different dye moiety, i. e., quinoline.

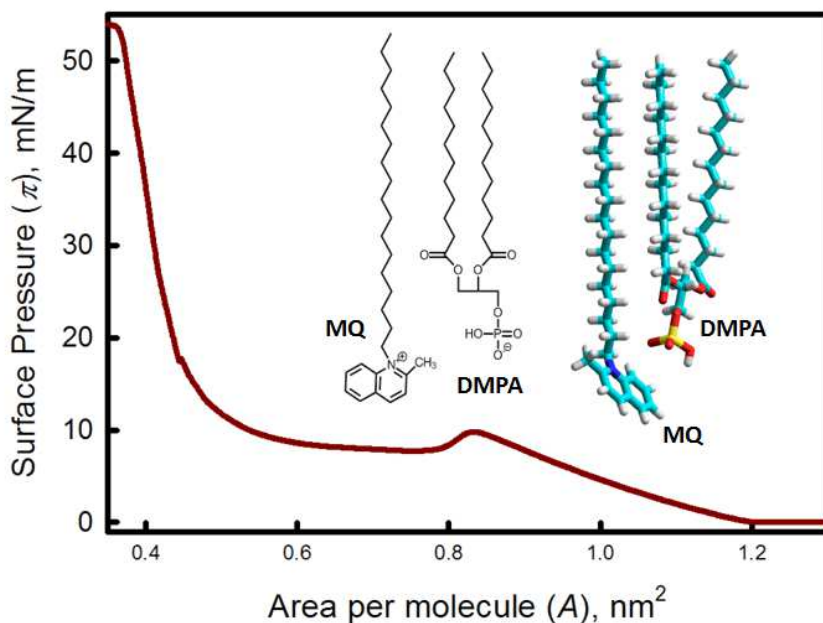


Figure 1.1: $\pi - A$ isotherm of the mixed monolayer MQ:DMPA = 1:1, the monolayer compression rate being $0.04\text{nm}^2\text{min}^{-1}\text{molecule}^{-1}$. Inset: Molecular structures of MQ and DMPA

Quinoline is a rather interesting chemical group for a number of applications. First and foremost, quinoline derivatives have a proven pharmaceutical activity.³³ Quinoline has also been used as a structural basis for electron transport materials in organic electronics³⁴ and ion sensing.³⁵ As previously observed for related monolayers, the components are completely

miscible due to ion-pair formation between them and to the good compatibility between hydrophobic regions. MQ is also a prochiral molecule as HSP. In the present study we try to analyze the influences that the polar group geometry of the monolayer cationic component has on the chiral structures geometry formed at the air-water interface. Thus, we observe that replacing the hemicyanine group by the methyl quinoline one leads to the formation of new chiral structures, confirming that the shape of the domains formed depends primarily on the geometry of the dye and its self-aggregation ability.

Two novel aspects are discussed herein with respect to the previous studies. First, an overshoot in the surface pressure has been observed in these mixed systems. This feature is typical to other systems where the attractive interactions between polar groups is strong, either through hydrogen bonding³⁶⁻³⁸ or self-aggregation.³⁹ A physical interpretation to this phenomenon is provided herein.

Second, for the MQ:DMPA mixed monolayers a great diversity in the shape and size of the domains is observed. The domain shapes and sizes for simple lipid monolayer can be understood phenomenologically by a competition between line tension at the domain boundary, and electrostatic dipole-dipole repulsions between molecules within and between domains.⁴⁰ Herein, however, dipole-dipole repulsion plays a secondary role, as a result of ion pair formation between DMPA and MQ. For the MQ:DMPA mixed system this phenomenon has been interpreted as due to the competition between two different growth mechanisms of the formed nuclei. We propose an experimental procedure to minimize one such mechanism, which leads to a homogeneous distribution in the shape and size of the domains.

1.2. Experimental Section

Materials: 2-methyl-1-octadecylquinoline (MQ) was synthesized by J. Sondermann at the Max-Planck-Institut für Biophysikalische Chemie.⁴¹ Dimyristoyl phosphatidic acid (DMPA) was purchased from Sigma-Aldrich and used as received. Phosphate potassium and acetate sodium salts were purchased from Sigma-Aldrich. A mixture of chloroform:methanol, ratio 3:1 (v/v), was used as the spreading solvent for dissolving both MQ and DMPA. The pure solvents were obtained from Aldrich and used without purification. Ultrapure water, produced by a Millipore Milli-Q unit, was pretreated by a Millipore reverse osmosis system (>18.2 MΩ/cm). The subphase temperature was 21 °C with pH 5.7. For both buffer solutions, the concentration of salt in each case was 0.001 M. The pH was adjusted to pH = 7.0 by adding dropwise a solution of 1M NaOH. The substrates used for LB transfer were cleaned as follows: successive steps with an alkaline detergent, isopropanol, and ethanol and then thoroughly rinsed with ultrapure water.

Isotherms of Langmuir films, and BAM imaging: A NIMA 601 trough (Nima Technology, Coventry, England) equipped with two symmetrical barriers to record BAM images was used. Images of the film morphology were obtained by Brewster angle microscopy (BAM) with a I-Elli2000 (Accurion GmbH, Göttingen, Germany) using a Nd:YAG diode laser with wavelength 532 nm and 50mW. The lateral resolution of the BAM microscope is 2 μm. The image processing procedure included a geometrical correction of the image as well as a filtering operation to reduce interference fringes and noise, with no additional treatment. No optical filters were applied during the BAM experiments. The polarizer and analyzer were set at 0° (p-configuration). The microscope and the film balance were located on a table with a vibration isolation (antivibration system MOD-2 S, Accurion GmbH, Göttingen, Germany) in a large class 100 clean room. Moreover, the Langmuir troughs and UV-vis reflection and BAM instruments were protected with a plastic case, ensuring no particulates that might still be present in the clean room could reach the air/liquid interface.

Langmuir-Schaefer films: The monolayers were transferred onto quartz substrates. The mixed monolayers were transferred by the Langmuir-Schaefer, i. e., by horizontal dipping at constant surface pressure. The multilayers were assembled by sequential monolayer transfer. The transfer ratio was close to unity for all transfer processes.

UV-visible electronic absorption spectra of the films were measured locating the substrate directly in the light path on a Cary 100 Bio UV-visible spectrophotometer.

Circular dichroism (CD) measurements were acquired using a Jasco J-715 CD spectrophotometer. All spectra were recorded at room temperature. The spectra were measured in the wavelength interval from 280 to 700 nm with a 0.2 nm step resolution and a 1 nm bandwidth. The scanning rate was 20 nm/min with 2 s response time. The signal-to-noise ratio was improved by accumulating 10 scans for each CD spectrum. Data processing was carried out using the J-700 software package. The blank spectrum of the bare quartz substrate was subtracted. To discard artifactual CD from birefringence effects or lineal dichroic contributions to the CD signal, BAM experiments with a systematic variation of the polarization angle were performed.⁴²

1.3. Results and Discussion

1.3.1. Surface pressure - Area isotherm

Figure 1.1 (red line) shows the π - A isotherm of the mixed monolayer MQ:DMPA in molar ratio 1:1. The take-off of the isotherm occurs at ~ 1.2 nm²/molecule, and a phase transition takes place at ~ 9 -10 mN/m. This phase transition involves a surface area reduction from ~ 0.85 nm² to ~ 0.5 nm². The monolayer collapse takes place at a surface pressure of ~ 54 mN/m, and an area per molecule of ca. 0.38 nm². When the monolayer is decompressed and a second compression process is realized no hysteresis was observed (see Figure SI.1.1 in Supporting Information).

The beginning of the phase transition takes place with an overshoot, (see Figure 1.1). The overshoot takes place for all values of the compression

rate monolayer tested, even for the slowest allowed by our experimental device, $0.04 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$. In this case, the overshoot coordinates are ca. 9.5 mN/m and 0.85 nm^2 per molecule. The drop in the surface pressure reaches ca. 2 mN/m after the overshoot is recorded. The overshoot is a function of the monolayer compression rate. The inset in Figure 1.2 shows the overshoot for different compression rates. With the increase of compression rate, the overshoot is shifted to a higher surface pressure and a lower surface area. The drop of the surface after the overshoot is reduced with the increase of the compression rate. Note that the region of the $\pi - A$ curves before the overshoot is not modified with different compression rates (see inset in Figure 1.2).

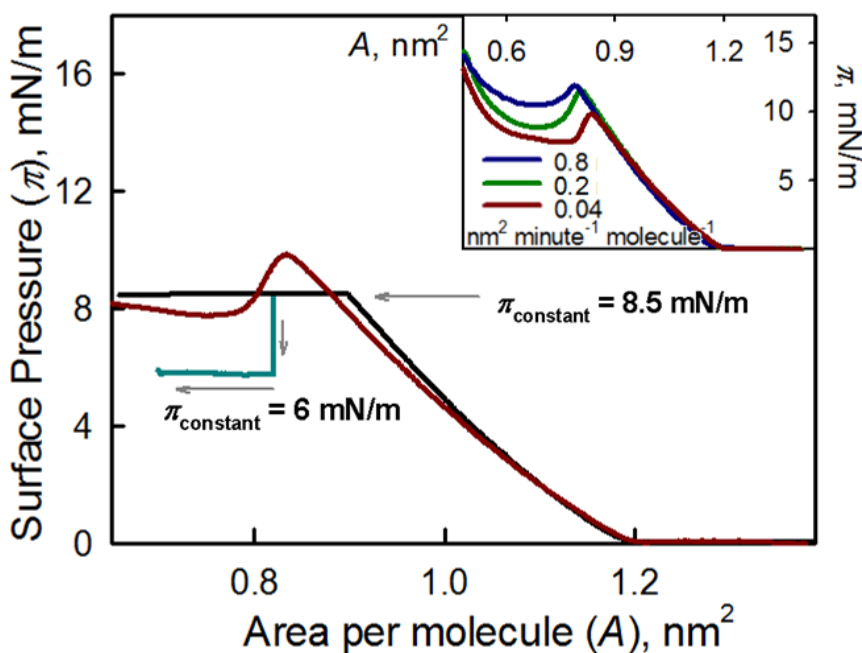


Figure 1.2: Red line: π - A isotherm of the mixed MQ:DMPA monolayer (compression rate $0.04 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$). Black line: evolution of surface area under an applied constant surface pressure of $\pi_{\text{constant}} = 8.5 \text{ mN/m}$. Blue line: evolution of surface area under an applied constant surface pressure of $\pi_{\text{constant}} = 8.5 \text{ mN/m}$, followed by $\pi_{\text{constant}} = 6 \text{ mN/m}$. Inset: $\pi - A$ isotherms for different compression rates as specified within the graph.

Vollhardt, and Fainerman⁴³ interpreted the overshoot in a surface pressure-molecular area isotherm as a *dynamic jump*. For these authors, the overshoot arises from the interplay between the kinetics of the monomer attachment to 2D aggregates and the growth of new nuclei.⁴³ On the other hand, herein we interpreted the overshoot as a consequence of a different phenomenon described as follows.

A nucleation process is usually composed of at least two different kinetic steps: nuclei formation and nuclei growth kinetics. These two kinetic steps might take place at different surface pressures, as observed by Vollhardt and Retter for 3D nucleation at the air/water interface.⁴⁴ The conclusions from that study can be generalized for 2D nucleation. The critical surface pressure required for the formation of nuclei (π_{crit}), and the minimum surface pressure at which the nuclei continue to grow (π_e) can be defined.⁴⁴ Herein, these two values of surface pressure have been experimentally assessed for the mixed monolayer MQ:DMPA. We propose that the overshoot in surface pressure occurs because $\pi_e < \pi_{\text{crit}}$.

For the π_{crit} measurement the surface pressure was kept constant at a previous point to the overshoot, noted as π_{constant} in Figure 1.2. In these experiments, the application of a surface pressure $\pi_{\text{constant}} < 8.5$ mN/m led to no relaxation of the monolayer. On the other hand, when $\pi_{\text{constant}} \geq 8.5$ mN/m, the monolayer begins to contract due to the feedback control system. In these cases the area relaxation is due to the nucleation and growth process at the monolayer. When $\pi_{\text{constant}} = 8.5$ mN/m, the surface area decreased from 0.9 nm² to 0.66 nm² per molecule, (see Figure 1.2). This area reduction took place within about 2 hours. Therefore, $\pi_{\text{crit}} \approx 8.5$ mN/m.

In a complementary experiment, nuclei were allowed to form at the constant surface pressure of 8.5 mN/m, until the overshoot was bypassed. At this point, a certain number of nuclei were formed, and the formation of new nuclei was interrupted by decreasing the surface pressure. For example, in Figure 1.2 the surface pressure was decreased to 6 mN/m (cyan line). The surface area occupied by the monolayer decreased, despite no new nuclei

being formed, (see Figure 1.2). This decrease in the surface area corresponded to the growth of existing nuclei. The area reduction in this case was from 0.82 nm² to 0.7 nm², area reduction, taking place within about 20 min. Control experiments applying a surface pressure below 6 mN/m led to a monolayer relaxation, thereby confirming that $\pi_e \approx 6$ mN/m.

The large difference between π_{crit} and π_e leads to the appearance of the overshoot in the surface pressure isotherm of the mixed monolayer MQ:DMPA. The small π_e value compared to π_{crit} , is related to the molecular interactions involved in the monolayer, which facilitate the incorporation of free molecules in preformed nuclei. First, the repulsive dipole-dipole interactions between neighboring molecules are minimized as a result of the ion pair formed between MQ and DMPA molecules. Second, the self-assembly of quinoline groups from MQ molecule also contributes to facilitate the incorporation of new molecules to the nuclei. These interactions are discussed below. This physical scenario can be applied to similar mixed monolayers at the air/water interface stabilized by different interactions, such as host-guest or hydrogen bonding.³⁶⁻³⁸

Figure SI.1.2 (Supporting Information) shows the π - A isotherms of mixed monolayers MQ:DMPA, obtained at various molar fractions of MQ. Note the isotherm overshoot could not be observed for a molar ration difference of 1:1. We therefore conclude the appearance of overshoot in the π - A isotherms of the mixed monolayers is evidence of the complete miscibility of the components MQ and DMPA. The sharp drop of π_e with respect to π_{crit} must be attributed to the strong molecular attraction between the monolayer components, which in turn facilitates the incorporation of molecules in preformed nuclei.

Additionally, some experiments for the mixed monolayer MQ:DMPA in molar ratio 1:1 by using phosphate or acetate buffered subphase (10⁻³ M) at pH = 7 were carried out. The π - A isotherms and BAM images do not show any relevant differences from those obtained by using unbuffered subphase. The null electrolyte influence in the aqueous subphase, at least at

concentrations of 0.001 M, indicates that ions cannot significantly affect the DMPA-MQ binding, due to the strength of this union.

1.3.2. Brewster Angle Microscopy (BAM)

Simultaneous to the isotherm recording, the morphology of the mixed monolayers was directly observed at the air-water interface by BAM. BAM images for two different experiences are shown in Figures 1.3 and 1.4, thus illustrating spontaneous variations in domain morphology. The same experimental protocol was carefully followed in both cases.

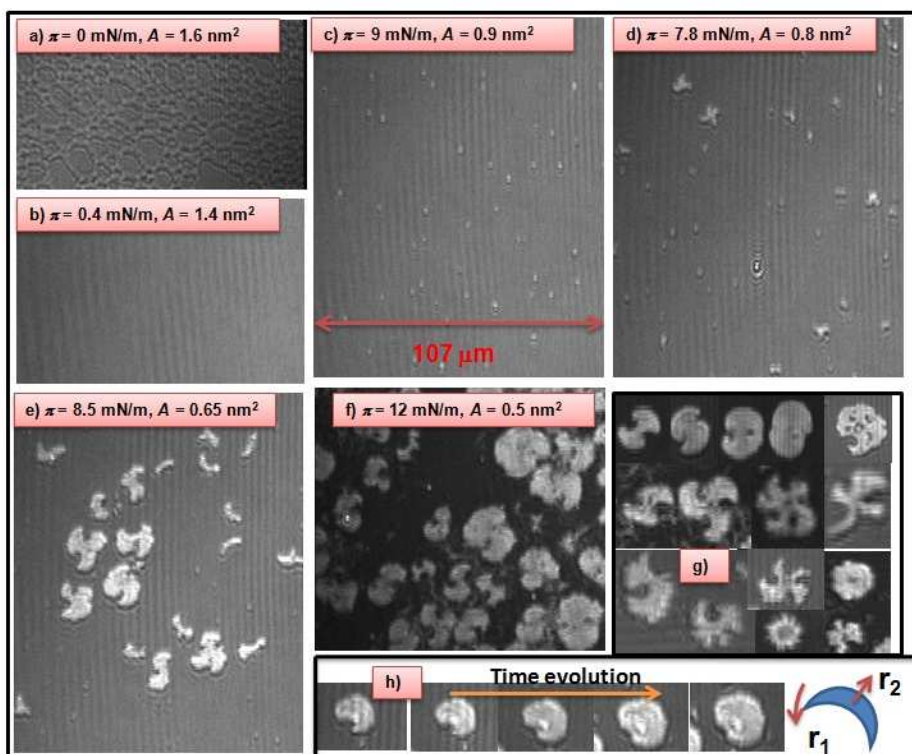


Figure 1.3: BAM images obtained along the compression process of the MQ:DMPA = 1:1 mixed monolayer. g) and h) do not preserve the scale indicated. h) Shows the time evolution of a domain as well as a scheme of two possible growth mechanisms of this domain, r_1 and r_2 .

This protocol included using freshly prepared solutions, waiting 30 minutes after spreading the mixture onto the interface and compressing at the lowest rate allowed by the Langmuir. In both experiments, the gas phase was observed for the surface area above the isotherm take off, (see Figure 1.3a). When an area of $1.4 \text{ nm}^2/\text{molecule}$ was reached, the monolayer appeared homogeneous (Fig 1.3b), and small bright spots began to appear close to the overshoot (see Figure.1.3c).

The bright spots density varied between different experiments, and even within the same experience large variations could be observed for different regions of the monolayer. Note that the monolayers were very fluid and constantly shifted under the BAM camera. After crossing the overshoot, the bright spots started growing(see Figure1.3d-f), resulting in domains with diverse shapes and sizes. Representative shapes of the observed domains are shown in Figure1.3g. We can observe bent strips shape domains or shaped blades domains with two, three, or more arms that twist in the same direction and that appear to emanate from a center. The spiral growth of these arms leads to structures that are closed on themselves, fusing the ends and resulting in a striking ring-shaped domains. In these domains a segment of non-condensed monolayer is enclosed by condensed monolayer(see Figures 1.3-g and 1.4). Figure 1.3h shows the change observed over time of a bent strip shape domain, where this domain grows and closes on itself.

In the experiment shown in Figure 1.4, the number of bright spots was much lower, so that the domain size is increased. Note that in Figure 1.4 the image width is twice the resolution of the images shown in Figure1.3. In this case, most are domains which are dog bone shaped such that the ends are bent in the same direction, indicating their chiral character. This chiral grows enough to coalesce through its sharp edges, giving the appearance of a circular domain, while still appreciating dark spots inside the domain. These dark spots correspond to the regions with a noncondensed monolayer. Thin arms are created and elongated from the edge of the nearly circular domains in the case of a surface pressure greater than $\pi > 10 \text{ mN/m}$ (see Figure. 1.4-e).

When the monolayer is compressed at high pressure the domains do not coalesce, deforming its edge (see Figure 1.4f). However, as previously shown, the sharp edges may coalesce when impinging on any other domain edge. It is noted that the domains display internal anisotropy, i. e., the vertical region appears darker than the horizontal region (Figure. 1.4d-f).

At surface pressure close to collapse (see Figure 1.4f) the air/water interface is covered with domains of the same composition, ruling out the possible segregation of components.

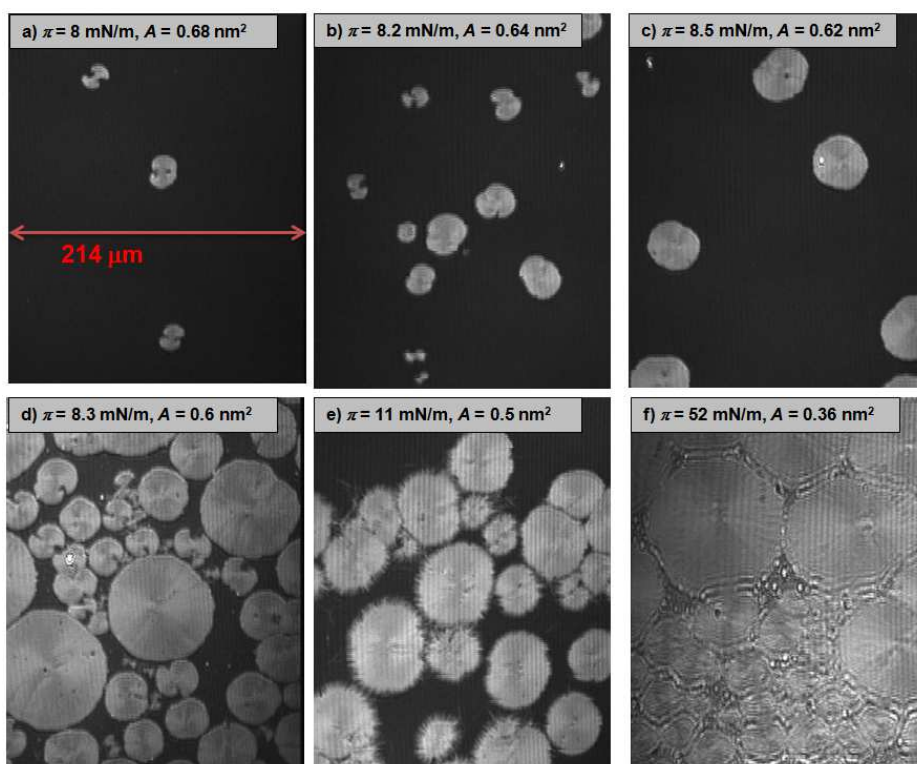


Figure 1.4: BAM images obtained along the compression process of the MQ:DMPA = 1:1 mixed monolayer.

The shape of the domains shown in Figures 1.3 and 1.4 indicated the formation of supramolecular chiral structures. Note that with the expansion of the monolayer, the initial state is again reached, and the domains disappear completely. Chiral structures on the air-water interface have been earlier

described for mixed monolayers formed by DMPA and a hemicyanine amphiphilic derivative.²⁹⁻³⁰ It was established that these structures were due to the aggregation of the hemicyanine group and were induced by the presence of a chiral group in the DMPA.²⁹

1.3.3. UV-Vis Reflection Spectroscopy (UVR) at the Air-Water Interface

The UV-vis reflection spectroscopy at the air/water interface allows obtaining in situ quantitative information on the presence and orientation of the chromophores at the interface. The UV-vis reflection spectroscopy is exclusively sensitive to the molecules existing at the air/water interface. Therefore, it discards any signal from the subphase.

For a Langmuir monolayer containing UV-vis absorbing molecules, the reflection of an incident light at the interface is enhanced by:⁴⁵⁻⁴⁷

$$\Delta R = R_{D,S} - R_S = 2.303 \times 10^3 f_o \varepsilon \sqrt{R_S} \Gamma \quad (1.1)$$

where R_S and $R_{D,S}$ are the reflectivity of the interface without and with the presence of the Langmuir monolayer, respectively. $R_S \approx 0.02$, and ε is the molar absorption coefficient with $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$ units, Γ is the surface concentration of the monolayer, with $\text{mol} \cdot \text{cm}^{-2}$ units, f_o is the orientation factor, which accounts for the preferred orientation of the transition dipole at the interface. The ε coefficient is obtained from bulk measurements, i. e., the MQ solution; therefore no preferred orientation is included.

However, anisotropy in the orientation of the dipoles is expected at the air/water interface. The orientation factor, f_o , accounts for the change in the absorption properties of the chromophore due to anisotropy. Given a non-degenerated absorption band, that is, with only one component of the transition dipole, the orientation factor is:⁴⁶

$$f_o = \frac{3}{2} \langle \sin^2(\theta) \rangle \quad (1.2)$$

where θ is the mean angle formed by the transition dipole and the normal axis to the air/water interface. Thus, a transition dipole orientation parallel with respect to the interface implies that $f_0 = 1.5$, whereas if the orientation is perpendicular, $f_0 = 0$. UV-vis reflection spectra are often expressed in normalized units in order to discard any additional effect to the variation of the surface concentration of the chromophore units at the interface.

The surface concentration of the dye molecule is expressed by $\Gamma = 10^{14}/(N_A \cdot A_{MQ})$, where N_A is the Avogadro number and A_{MQ} is the molecular area of MQ. A_{MQ} is obtained from the π -A isotherms by $A_{MQ} = 2 \cdot A_{TOTAL}$. The normalized reflection signal is the product of the absolute reflection signal by the molecular area of the chromophore:

$$\Delta R_{\text{norm}} = A_{MQ} \times \Delta R = \frac{2.303 \times 10^{17} f_0 \epsilon}{N_A} \sqrt{R_s} = 5.41 \times 10^{-8} f_0 \epsilon \quad (1.3)$$

ΔR_{norm} has $\text{nm}^2 \cdot \text{molec}^{-1}$ units. The normalized reflection spectra offer plural information on molecular aggregation as well as on molecular orientation.

Figure 1.5 shows the UV-vis reflection spectra for the MQ:DMPA mixed monolayer at different surface areas. For comparison, the UV-vis absorption spectrum of the MQ molecule in solution is also included (black dotted line).

In the solution spectrum three absorption peaks can be observed, whose wavelengths and ϵ values are; $\lambda_1 = 321 \text{ nm}$ ($\epsilon_1 = 1.34 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), $\lambda_2 = 312 \text{ nm}$ ($\epsilon_2 = 1.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and $\lambda_3 = 242 \text{ nm}$ ($\epsilon_3 = 4.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The directions of the transition dipoles have been theoretically calculated for these absorption components, see Supporting Information. The transition dipoles of λ_2 and λ_3 absorbing components are oriented along the A axis of the molecule, see inset in Figure 1.5. On the other hand, the λ_1 component is directed along the B axis, which is rotated 48° to the previous axis. Both A and B axes are located in the quinoline group plane.

The normalized reflection spectrum before the formation of domains and bright spots observed by BAM at $A = 1.1 \text{ nm}^2$ is shown in Figure 1.5 (red line). The shape of this reflection spectrum is almost coincident with the absorption spectrum in solution, i.e. the relationship between the band heights is identical to that observed in bulk solution. Because of the different orientation of A and B axes, this behavior can only be explained in two extreme situations: the quinoline group is randomly oriented with respect to the interface, as in solution, which is highly unlikely given the amphiphilic character of the molecule, or the quinoline group plane is positioned parallel to the air-water interface, in this case keeping the relative height between the bands. The latter can be confirmed from the following: using the value $\epsilon_3 = 4.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in equation (1.3) and $f_0 = 1.5$ (parallel orientation with respect to the interface), $\Delta R_{\text{norm}} \times 100 = 0.346 \text{ nm}^2$ is obtained, almost matching the value with that obtained experimentally (0.35). The same agreement is obtained with other bands, confirming that at low surface pressures the quinoline group is placed with its plane parallel to the interface.

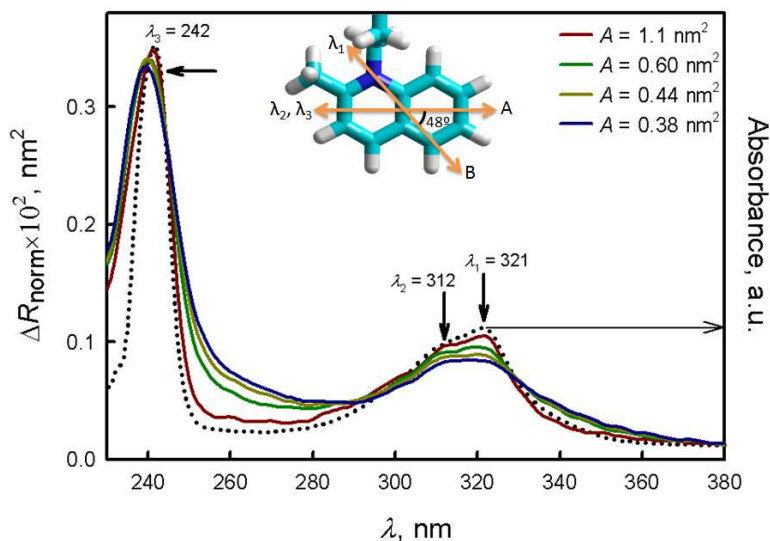


Figure 1.5: UV-vis reflection spectra of the MQ:DMPA mixed monolayer at different surface areas. The UV-vis spectrum of MQ in bulk solution (chloroform : methanol, ratio 3.1 (v/v)) is included for comparison (black dotted line). Inset: A and B absorption axis for the methyl quinoline group.

As the surface pressure increases and decreases the surface area (see Figure 1.5), the band corresponding to the λ_3 mode shifts to shorter wavelengths up to 238 nm, which can be related to the H type aggregate. However, the λ_1 and λ_2 modes do not show significant displacement of wavelength. This phenomenon is due to the lesser oscillator strength of these components, and will be further analyzed below.

Likewise, Figure 1.5 shows that as the surface area decreases the intensity of the λ_1 mode decreases with respect to other absorption modes. This fact should be related to the tilt of the quinoline B axis (see Figure 1.5), while the A axis must remain almost parallel to the interface. A quantification of this phenomenon at a high surface pressure, via equation (1.3), permits us to calculate $f_0 \approx 1.1$ at $\pi = 40$ mN / m, for λ_1 mode.

1.3.4. Circular Dichroism (CD) Spectroscopy.

The shape of the domains observed by BAM suggests the formation of chiral supramolecular structures. Helix-shaped structures, or branches that all rotate in the same direction, are observed, (see Figure 1.3g). To assess the existence of chirality in the mixed monolayer MQ:DMPA, these monolayers were transferred to solid supports to perform circular dichroism (CD) spectrometry.

The monolayers were transferred onto a quartz substrate at $\pi = 30$ mN/m by the horizontal lifting or Langmuir-Schaefer (LS) method. The transmission spectrum of 5 LS monolayers is shown in Figure 1.6a. The reflection and transmission spectra do not show significant differences. Therefore, any change on the organization of the MQ headgroup during the transfer process is discarded. The absence of the reorganization process during transfer is important concerning the validity of the CD results. Figure 1.6b shows two CD spectra of 5 LS monolayers. The red line corresponds to a condition in which there is a homogeneous distribution of domains, as discussed below, while the green line corresponds to conditions where there is

a heterogeneous distribution of domains, see (Figure 1.3-1.4). Small differences between the two spectra have been observed.

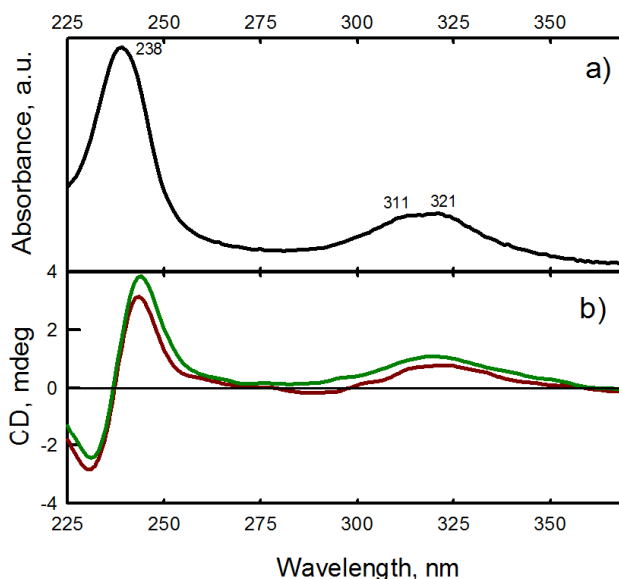


Figure 1.6: a) UV transmission spectrum of 5 LS films of the MQ:DMPA system. b) CD spectrum of 5 LS films in which there is a homogeneous distribution of domains (red line) and with a heterogeneous distribution of domains (green line).

To discard artifactual CD from birefringence effects or lineal dichroic contributions to the CD signal, the method proposed by Spitz et al. was applied.⁴² The CD spectra showed the characteristic bisignate signals only for the 238 nm band (maximum at 244 nm and minimum at 230 nm) with a crossover at ~ 237 nm, close to the absorption maximum. However, for the 321-312 nm bands, the CD signals showed a positive sign exclusively, with a maximum at 320 nm. The bisignate signal observed for the CD spectrum (238 nm band) is indicative of an intense exciton coupled between the transition dipoles of adjacent molecules.⁴⁸ However, the fact that only positive Cotton effect was observed in the CD spectra for the 321-312 nm band should be indicative of low exciton coupling due to the smaller transition dipoles of these components.

Therefore, the chirality should be related to the formation of chiral supramolecular aggregation of MQ polar group. The existence of chiral domains with arms that are twisted in the same direction is a consequence of the MQ aggregation at molecular level.

Further experiments were made by modifying the number of transferred monolayers. In all the experiences the form of the CD signal obtained was always the same, and there were no observed changes in the sign of the CD peaks, indicating that chirality is not caused by a spontaneous breaking of symmetry, which would create spectra complementary with sign changes.

1.3.5. Molecular Mechanics Study for the Quinoline Group Rearrangement at the Air/Water Interface.

UV-visible Reflection spectra at the air-water interface showed that λ_1 and λ_2 modes did not show wavelength shift, while the λ_3 mode shifted 4 nm to blue, when the surface pressure increased (see Figure 1.5). This behavior seemed to indicate a null or small molecular aggregation of the quinoline group. However, the CD spectra clearly indicate the formation of supramolecular chiral aggregates when monolayers were transferred from the air-water interface to the solid support. To obtain additional information on the aggregate rearrangement, theoretical studies using molecular mechanics have been performed.

The quantum semiempirical method RM1⁴⁹ has been used to optimize MQ⁺ and DMPA⁻ molecules separately. The evolution of 4 units of the MQ:DMPA pair has been subsequently studied. In each simulation we have used only one of the MQ prochiral enantiomers. The initial position comprises the quinoline groups stacked, and with a separation distance of ca. 0.4-0.5 nm. DMPA molecules were distributed on the sides of this structure. Next, the geometry was optimized using MM+, and three runs of the molecular dynamic simulations were performed to search for possible existence of structures with lower energy. Each run consisted of heating the structure to

300 K, molecular dynamics simulations for 5 ps, and then annealing to 0 K. Finally, the geometry was again optimized using MM+. Note that the calculations are performed *in vacuo*, i. e., in absence of water molecules and other interacting molecules. The results offer semiquantitative valuable insights into the rearrangement at the molecular level but must be used with some caution.

Figure 1.7A shows the final frame for one of the calculations. DMPA molecules are represented in purple, the hydrogens are not shown for simplicity. Figure 1.7B,C shows only the final position of the quinoline groups. Figure 1.7B shows the four quinoline groups from a side perspective. In this case, the plane rotation of these groups is clearly observed. Figure 1.7C shows two consecutive quinoline groups, one colored in green. From a frontal perspective, we can also observe the rotation of the molecule plane.

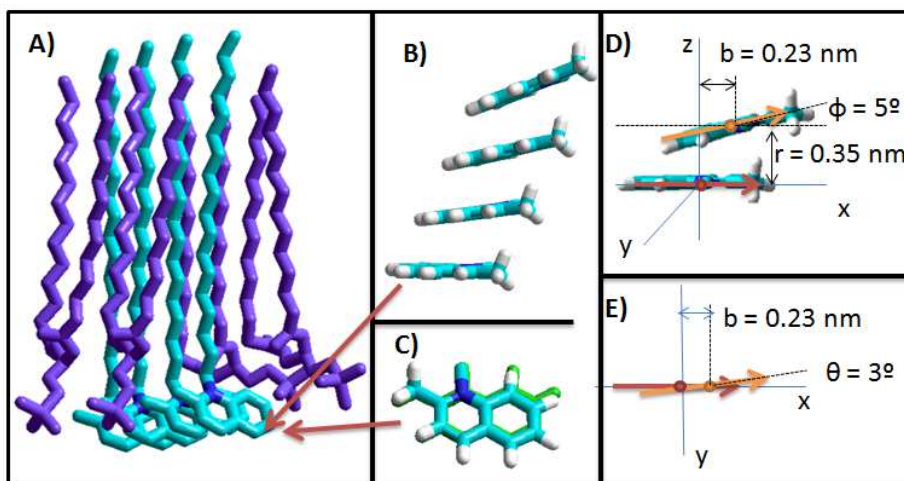


Figure 1.7. A) Final frame for one of the MM+ calculations. DMPA molecules are represented in purple, and the hydrogens are not shown for simplicity. B) Side perspective where only the four quinoline groups are shown. C) Frontal perspective of two consecutive quinoline groups. D) Side and E) frontal average distribution of two consecutive quinoline groups. The red and orange arrows represent the transition dipoles of two consecutive molecules.

MM+ simulation shows us that three types of intermolecular interactions are most significant in the formation of mixed DMPA:MQ monolayers: a) electrostatic between the polar heads of DMPA and MQ, b) self-aggregation between the quinoline groups, and c) hydrophobic between the alkyl chains of both components. Moreover, when initially setting a prochiral enantiomer of MQ in the presence of DMPA, chiral structures are formed, as observed experimentally. Those three interactions must contribute cooperatively to the formation of chiral structures. Unfortunately, MM+ simulation does not offer any information on the pathway to formation of chiral domains or the specific role of DMPA on symmetry breaking, if any.

The blue shift of the λ_3 MQ absorption band can be quantitatively interpreted using the extended dipole model.^{46,50-53} By this approximation, the molecules are replaced by their transition dipoles. For the application of this model, it is necessary to know the separation and relative orientation of the chromophores (quinoline groups). Figures 1.7D and 1.7E show the distribution used, as a result of averaging the determined parameters after five different computations runs. The red and orange arrows represent the transition dipoles of two consecutive molecules.

From the relative arrangement of the consecutive quinoline groups shown in Figures 1.7D and 1.7E, and after the extended dipole model application, supposing the formation of an infinite aggregate, we obtain a blue shift of 4 nm for the λ_3 mode, in excellent agreement with the experimental data. Similar calculations using the λ_1 and λ_2 modes lead to maximum wavelength displacement lower than 2 nm. Details about the extended dipole application are given in the Supporting Information.

This band displacement originates from the molecular aggregation, depending on the relative molecular arrangement, aggregation number, and oscillator strength of the band. In this sense, the molecular distribution obtained from calculations using molecular mechanics is able to explain the formation of chiral structures and the small shifts observed in the absorption bands of the quinoline group.

1.3.6. Control over the Shape and Size of the Chiral Domains Observed by BAM

A number of experiments have been conducted to determine the origin of diversity in the size and shape of the domains observed by BAM. We have observed that using freshly prepared solutions and allowing a waiting time before compressing the monolayer of ca. 45 minutes ensure a good reproducibility of the results. However, no homogeneous domain distributions were observed in any experiment. Additional experimental parameters have been analyzed, e. g., spreading solvent and concentration and temperature. The variation in these experimental parameters does not produce significant variations in results, as shown in Figures 1.3 and 1.4.

The heterogeneous distribution of size and shape in the domains is related with the small local fluctuations in the surface pressure, arising from the fluid flow at the air/liquid interface.⁵⁴⁻⁵⁵ The local heterogeneities at the air/liquid interface can lead to heterogeneous distribution of nuclei. However, in our system, the growth and evolution of the chiral mesoscopic domains are analyzed in terms of the geometrical type of edge regions of a given domain. The edge regions of a chiral domain can be classified into three types: concave, convex and sharp. One of the main features of a chiral domain is the dependence of the growth rate with the edge curvatures. Chiral domains do not display a significant growth of concave regions, while the convex and sharp edges might have growth. For pure spiral-type domains, only the sharp-edged regions can grow. However, in our case the domain grows through its sharp edge (r_1) and its convex edge (r_2) and closes on itself, as shown in the domain evolution (see Figure 1.3h). The domain growth through its convex and sharp edges is also shown, as the sharp edges coalesce when impinging on any other domain edge. However, the convex and concave edges do not coalesce when impinging on each other (see Figure 1.4f).

According to our results, the great diversity in the size and shape of the domains is strongly influenced by the competition between the two growth mechanisms of the nuclei, r_1 and r_2 . Therefore, the tuning of the growth of the

domains requires specific influence on the r_1 and r_2 mechanisms, eliminating or enhancing any of these.

The growth through the convex edge of the domains, defined as r_2 , can be minimized as follows: Alternated steps, at which a constant rate of compression is fixed, with periods where a constant surface pressure is applied. This procedure is illustrated in Figure 1.8, where the π - A (red line) and A - t (blue line) curves for a given experiment are shown. The procedure has 4 steps. Detailed values of experimental parameters are provided in the Supporting Information. The 4 steps are defined as follows:

(1) The monolayer is compressed at a slow compression rate until a surface pressure is reached between π_{crit} and π_e , as displayed in Figure 1.8 from A to B. (2) Surface pressure is kept constant for a certain period of time of ca. 30 minutes, (see Figure 1.8 from B to C). (3) The monolayer is compressed again but now at a high compression rate just to a surface pressure beyond the overshoot. This step is shown in Figure 1.8 as C to D. Rapid growth of the nuclei through its sharp edges against the r_2 growth process is induced here. The nuclei are then distributed homogeneously over the air/liquid interface, though local inhomogeneity can still exist. (4) The surface pressure is fastly decreased to a new constant value, of ca. 6-8 mN/m, above π_e . The relaxation of the mixed monolayer is then allowed (see D to F in Figure 1.8). This step takes place in two stages, first from D to E, where the barrier expands due to the dissolution of nuclei with a size below the critical one. This stage lasts ca. 12 s. In the second stage, once the input surface pressure is reached, the monolayer begins to contract due to the feedback control system, segment E to F.

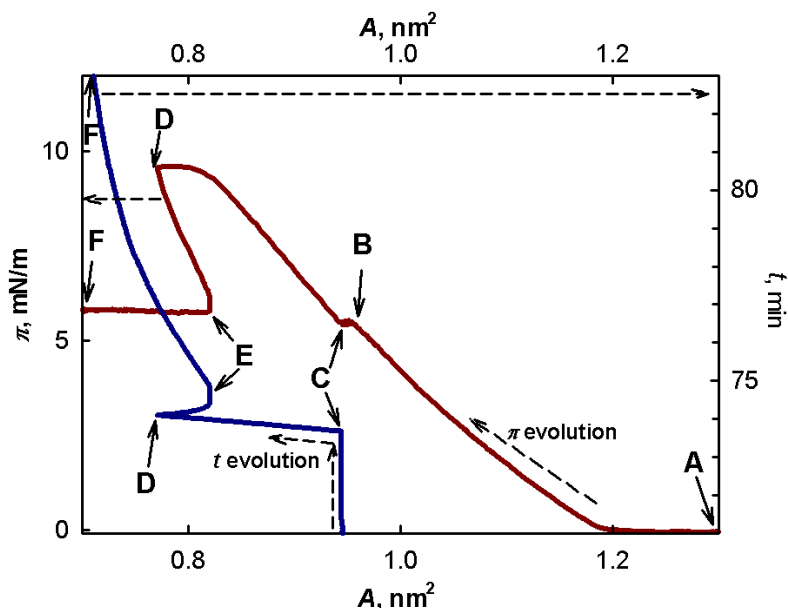


Figure 1.8. π - A (Red line) and A - t (blue line) of the mixed Langmuir monolayer MQ:DMPA. A-B Segment: Compression rate $0.04 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$. B-C Segment: The surface pressure is kept constant at 6 mN/m . C-D Segment: Compression rate $0.8 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$. D-E-F Segment: The surface pressure is kept constant at 6 mN/m . The D-E segment corresponds to the elapsed time for adapting the instrument.

BAM images corresponding to the mixed monolayer subjected to the described procedure are shown in Figure 1.9 a-c. No domains were observed along steps 1 and 2. Nuclei grew very quickly upon step 3. The nuclei grew into elongated structures that folded up to complete circle- or spiral-like domains. In addition to these elongated structures, many small spots could be observed, indicating that new nuclei continued forming (Figure 1.9a). After applying step 4, only circular domains displaying on inner dark region appear (Figure 1.9b). The small spot domains disappeared, possibly being dissolved due to the fast decrease of the surface pressure. Further evolution of the domains during step 4 led to growth of the domains from their perimeter. The domains were homogeneously distributed, having a similar size and shape of ring-like structures with arms arising from the central ring. A certain hexagonal ordering of the domains at the air/liquid interface was also obtained (see Figure 1.9c).

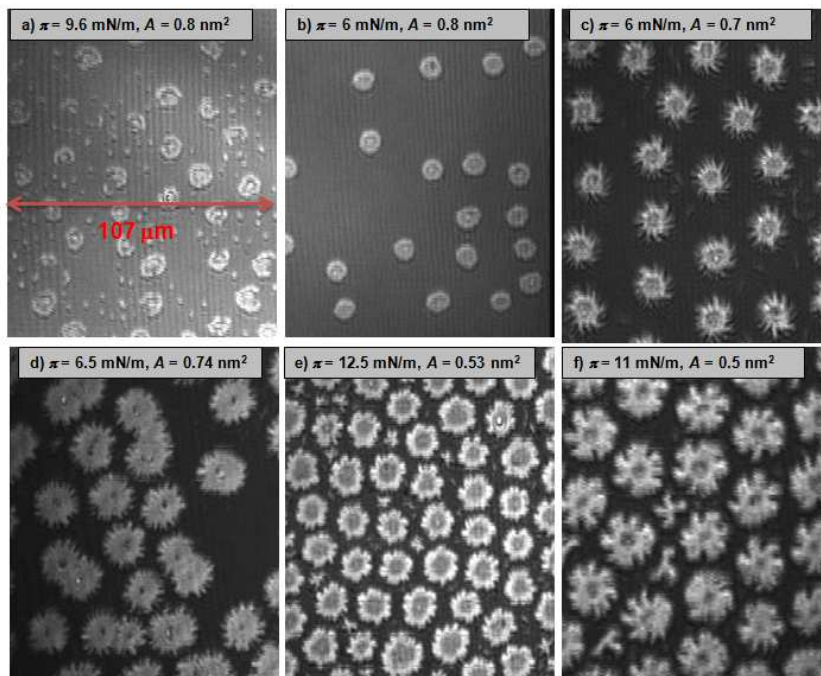


Figure 1.9: a-c: Evolution of domains during the application of the sequence of surface pressure described in Figure 1.8. d-f) Domains obtained when the applied surface pressure in steps 3) and 4) are modified. See Supporting Information for details on the values of surface pressure.

Different values of surface pressure can be applied in steps 3 and 4, (see Supporting Information for detailed values). In such a case, domains with ring shapes and arms pointing out from the central core of the domains, and flower-like or cogwheel shaped, are also obtained, (see Figure 1.9d-f).

Note this experimental procedure has been inspired by the electrochemical prepulse method, which is used to study the 2D and 3D electrochemical phase transitions.⁵⁶ In this method, a high overpotential is applied initially for a short time period to allow a homogeneous nuclei formation, which follows the application of a lower overpotential for which only the nuclei growth is allowed, enabling the measurement of the nuclei growth rate with no dependence on the nuclei formation rate.

The extent of homogeneity in the distribution of domain size and shape does not affect the UV-vis and CD spectra of the mixed MQ:DMPA monolayers, as shown above. We therefore conclude that the CD signal is not affected by the domain geometry and size in the mesoscale. The coherent molecular aggregate of the HQ headgroups takes place in a smaller scale, i. e., nanometric.

Remarkably, the occurrence of the different domain shapes is completely dependent on the sequence of applied surface pressure steps that are performed on the mixed Langmuir monolayer. The intermolecular interactions between the MQ and DMPA molecules are necessary for the stability of the mixed Langmuir monolayer at the air/liquid interface.^{40,57} However, the final shape of the domain in the mesoscale is not exclusively based on molecular interactions, but kinetic factors are also involved.

1.4. Conclusions

The mixed Langmuir monolayers formed by an anionic phospholipid, DMPA, and a cationic amphiphilic quinoline derivative, MQ, in a molar ratio 1:1, have been studied. Both MQ and DMPA molecules have a good compatibility between their hydrophilic and hydrophobic regions, leading to completely homogeneous mixtures when components are cospread on the air-water interface.

Remarkably, an overshoot at the beginning of the phase transition that takes place in the π - A isotherms of this mixed monolayer appears. This overshoot is interpreted as follows: The nucleation process associated to a phase transition is caused by at least 2 different kinetics. The first process corresponds to the nuclei formation, which starts at a surface pressure π_{crit} .⁴⁴ The second kinetics corresponds to the nuclei growth rate, which starts from a certain superficial pressure π_e .⁴⁴ When $\pi_{\text{crit}} \approx \pi_e$, the phase transition is characterized by a plateau in the π - A isotherm. However, when $\pi_{\text{crit}} > \pi_e$, and after the nuclei formation (π_{crit}), a sharp decrease in surface pressure can take place, until a new equilibrium value is reached (π_e). The magnitude of this

decrease depends on the difference between both surface pressure and the relative rates of these processes with respect to the monolayer compression rate. In the mixed monolayer MQ: DMPA, the overshoot can be originated from the large difference between both surface pressures. According to our results, the rather small π_e value compared to π_{crit} , must be attributed to the molecular interactions involved in the mixed monolayer, which facilitate the incorporation of molecules in preformed nuclei. These molecular interactions are mainly based on the formation of an ionic pair between the MQ and DMPA molecules as well as on the self-assembly of quinoline groups from the MQ molecule. Therefore, we propose that the appearance of overshoots in the π - A isotherms of the mixed monolayers is evidence of the complete miscibility of the MQ and DMPA molecules at the air-water interface.

Another remarkable phenomenon for this mixed monolayer is the formation of the chiral domains at the air-water interface. These chiral domains show a great diversity of shapes and sizes, (see Figures 1.3 and 1.4). The chirality is confirmed by CD spectrometry, being related to the formation of the chiral supramolecular aggregation of the MQ polar group. The existence of chiral domains at the air-water interface is a consequence of the MQ aggregation at molecular level. In all the experiments the form of the CD signal obtained was always the same. So, there were no observed changes in the sign of the CD peaks, indicating that chirality was not caused by a spontaneous breaking of symmetry, which would create spectra complementary with sign changes.⁶ The same behavior was observed in DMPA:HSP mixed monolayer, i.e, only a chiral aggregate was observed.²⁹ In this case control experiments using racemic DMPG instead of DMPA resulted in formation of both enantiomer structures. We therefore concluded that the phospholipid plays a critical role in the formation of the chiral structure.²⁹ In the case of racémica DMPG:MQ = 1:1 mixed monolayers, circular domains were formed, but in any case chiral structures were observed (data not shown). We ascribe this difference to the bulkier DMPG polar group compared to DMPA, which somehow might prevent the formation of chiral

structures in this case. Due to the similarity between HSP:DMPA and MQ:DMPA systems, we propose that the breaking of symmetry must be induced by the presence of a chiral group in the DMPA.

Theoretical simulations using molecular mechanics confirm the strong trend of the quinoline group to form chiral aggregates. The extended dipole model has also been applied⁵⁰⁻⁵¹ to verify whether the chiral structures rearrangement is compatible with the wavelength displacement of the MQ absorption bands observed at the air-water interface. In this sense, the molecular distribution obtained from calculations using molecular mechanics, allows us to explain the formation of chiral structures and the wavelength shifts observed in the absorption bands of the quinoline group.

Additionally, we have observed that the chiral domains of the MQ:DMPA mixed monolayers grow through its sharp edge (r_1) and its convex edge (r_2). In our opinion, the great diversity in the size and shape of the domains observed by BAM for this system is strongly influenced by the competition between these two mechanisms. The drop in surface pressure after the overshoot results in the rate of these processes becoming competitive. In this way, it is possible to control the domain size and shape, eliminating or enhancing any of these processes specifically. Thus, we propose an experimental procedure which permits us to minimize the growth through the convex edge of the domains, defined as r_2 . In this way, a homogeneous domain distribution with ring shape structures and with arms arising from the central ring (flowers or cogwheel shaped) can be obtained (see Figure 1.9). In this way we prove that the occurrence of the different domain shapes is dependent on the sequence of applied surface pressure steps that are performed on the mixed Langmuir monolayer and that the final shape of the domain in the mesoscale is not exclusively based on molecular interactions, but kinetic factors associated to the nucleation process are involved as well.

In summary, the formation of chiral domains by the mixed monolayer arises from a complex and delicate interplay between three types of

interactions: (1) electrostatic between DMPA and MQ, 2) self-aggregation between quinoline groups, and c) hydrophobic between alkyl chains. These three interactions must contribute cooperatively to the formation of chiral structures. The ion-pair and the good compatibility between hydrophobic regions contributes to the stability of the mixed Langmuir monolayer, additionally allowing the quinoline group to have enough spatial freedom to form chiral aggregates. Moreover, this chirality is not caused by a spontaneous breaking of symmetry because only one enantiomeric assembly could be observed. We propose that the optical isomer L-DMPA induces the chirality on the domains, in a similar way as occurs in the DMPA:HSP system.²⁹

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1.5. Supporting Information

1.5.1. Experimental and theoretical detailed procedures.

1.5.1.1 Extended dipole model.

The extended dipole model requires the assumption of considering molecules as their transition dipoles, $\mu = l \times q$, with fixed dipole length (l) and charge (q).¹⁻⁵

Formation of infinite lineal aggregates of the HQ polar headgroups is assumed. Within these aggregates, the relative arrangement of two neighbors HQ groups is calculated from the final result of the molecular mechanics simulation. Figures 1.7D and 1.7E in the paper show the distribution used, result of averaging the determined parameters after 5 different computations. The red and orange arrows represent the transition dipoles of two consecutive molecules.

Given a quinoleine reference molecule, 1, the average excitation energy of this molecule due to the aggregation with N neighbor MQ molecules can be expressed as;

$$\Delta E_N = \Delta E_{mon} + 2 \sum_{i=2}^N J_{1i} \frac{2(N+1-i)}{N} \quad (\text{SI-1.1})$$

where ΔE_{mon} is the excitation energy of the MQ monomer, and J_{1i} is the interaction energy between the dipoles corresponding to the reference molecule and each i molecules of the lineal aggregate, which can be expressed in an approximately way by;

$$J_{1i} = \frac{q^2}{D} \left[\frac{1}{a_{1i}} + \frac{1}{b_{1i}} - \frac{1}{c_{1i}} - \frac{1}{d_{1i}} \right] \quad (\text{SI-1.2})$$

$D \approx 2.5$ the dielectric constant, and a_{1i} , b_{1i} , c_{1i} and d_{1i} are the distances between ends of the dipoles positive–positive, negative–negative, positive–negative and negative–positive, respectively. Thus, the maximum wavelength of the aggregate λ_N , is;

$$\lambda_N = \frac{\lambda_{mon} hc 10^7}{hc 10^7 + 4 \sum_{i=2}^N J_{1i} \frac{(N+1-i)}{N}} \quad (\text{SI-1.3})$$

For the λ_3 mode $\lambda_{mon} = 242$ nm the maximum wavelength of monomer, i.e., in absence of aggregation. The application of this model requires the previous knowledge of l , q , and μ . The value $\mu = l \times q = 5.17$ Debye for the transition dipole that has been obtained by integrating the absorption band in solution (oscillator strength, $f = 0.329$). When $N \rightarrow \infty$ and $l = 0.3$ nm and $q = 0.36$ e, $\lambda_N = 238$ nm is obtained, in good agreement with the experimental data, see Figure 1.5 in the paper. Similar calculations using the λ_1 and λ_2 modes lead to maximum wavelength displacement lower than 2 nm.

1.5.1.2. Experimental parameters for tuning the shape and size of the chiral domains.

We have observed that using freshly prepared solutions, and allowing a waiting time before compressing the monolayer of 45 minutes, assures a good reproducibility of the results. No homogeneous domains distribution was obtained in any experiment. Additional experimental parameters have been analyzed: spreading solvent, concentration of spreading solution, and temperature of the liquid subphase. The variation in these experimental parameters does not lead to significant changes in the experimental results, as shown in Figures 1.3 and 1.4 of the paper. Note that during the phase transition the monolayer moves quickly under the BAM focus, thus the evolution of the domains is difficult to be followed in great detail.

Experimental parameters for the results showed in Figure 1.8 and 1.9 of the paper are defined as follows;

Compression rate ($\text{nm}^2 \text{min}^{-1} \text{molecule}^{-1}$)

Slow 0.04

Fast 0.80

Point	Figure 1.8 and Figures 1.9a-1.9c	Figure 1.9-d	Figure 1.9-e	Figure 1.9-f
B (π , mN/m)	6	6	6	6
D (π , mN/m)	9.5	11	12	9.5
E (π , mN/m)	6	6.5	7	7

1.5.2. Cyclic isotherms

Figure SI.1.1 (red line) shows the π - A isotherms of MQ:DMPA system during the first compression cycle. When the monolayer is decompressed (gray line), and a second compression process is realized (black dotted line) no hysteresis was observed.

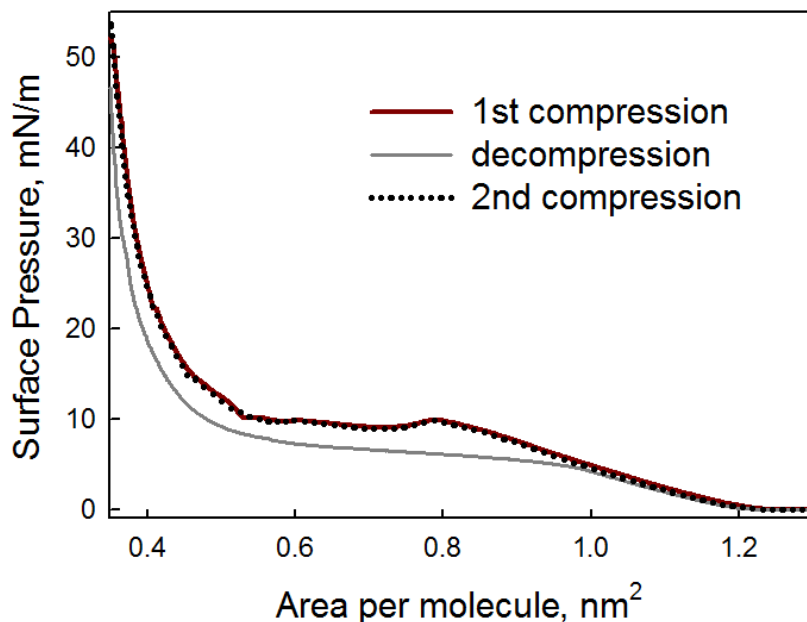


Figure SI.1.1. Surface pressure-area (π - A) isotherms of the mixed MQ:DMPA monolayer. Red line: first compression cycle. Gray line: decompression process. Black dotted line: Second compression cycle. $T = 21^\circ\text{C}$.

1.5.3. Variation of molar ratio MQ:DMPA in mixed Langmuir monolayers.

Figure SI.1.2 shows the π - A isotherms of MQ:DMPA monolayers, obtained at various molar fractions of MQ. It has to be pointed out that the isotherm overshoot could not be observed for $x \neq 0.5$.

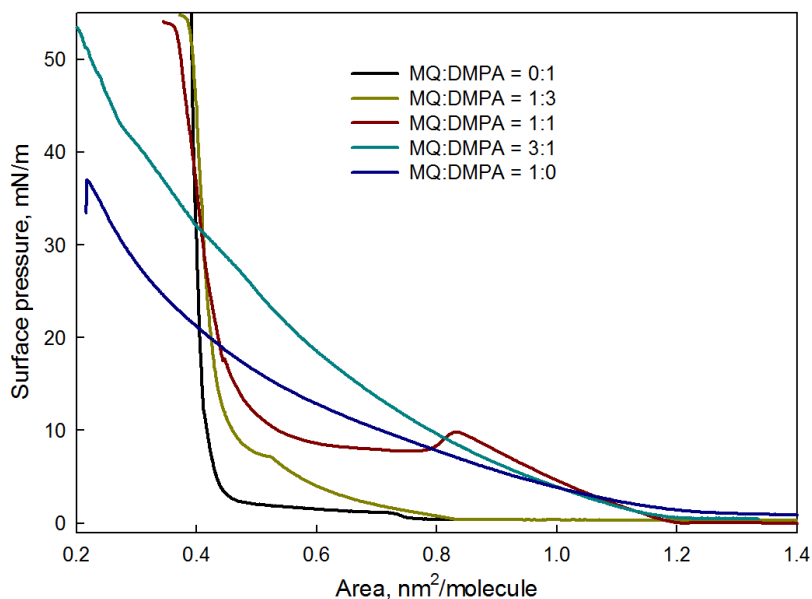


Figure SI.1.2. Surface pressure-area (π -A) isotherms of the mixed MQ:DMPA monolayer at various mole fractions of MQ(x) at T = 21°C.

1.5.4. UV-Visible spectrum Simulation and bands assignment.

In order to simulate the MQ UV-Visible spectrum and obtain the transition dipoles orientation, the geometry molecule was previously optimized by using the RM1 semi-empirical method.⁶ Then, the UV-Visible spectrum was simulated in vacuum, using the ZINDO/S-CI semi-empirical method,⁷ with $OWP_{\pi-\pi} = 0.58$ (Overlap Weighting Factor). This semi-empirical method is designed to reproduce UV-Visible spectra of organic molecules, showing an accuracy similar to the Density Functional methods.⁸ Both calculations were performed using the commercial software Hyperchem 8.0.⁹

By this procedure the transitions between the 8 OM occupied of highest energy and 8 OM unoccupied of lower energy were obtained. In this simulation a total of 128 possible transitions, 64 singlets ($\Delta S=0$) and 64 triplets ($\Delta S=1$) were analyzed. Of these transitions only 3 have wavelength $\lambda_{\max} > 240$ nm, and oscillator strength different of zero (allowed transitions) which are shown in Figure SI.1.3. These transitions correspond to the modes λ_1 , λ_2 and λ_3 , observed in the experimental spectrum.

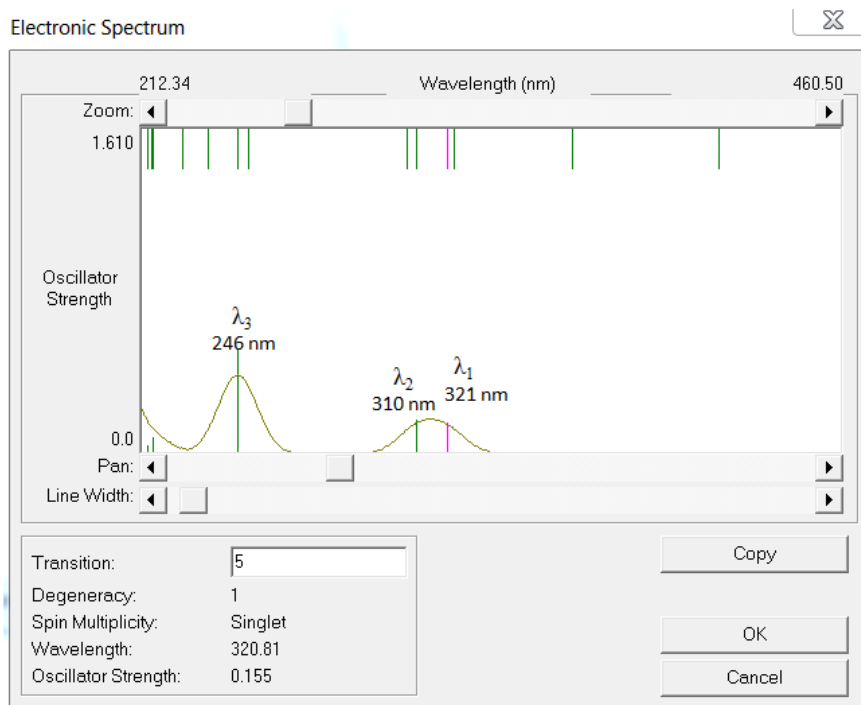


Figure SI.1.3: *In vacuo* simulated UV-Vis spectrum of MQ by using Hyperchem

8.0.

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2. Aggregation and Structural Study of the Monolayers Formed by an Amphiphilic Thiapenta- Carbocyanine

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Exotic assemblies with unique photophysical features can be built based on organic dyes at the air-liquid interface. Langmuir monolayers of N,N'-dioctadecylthiapentacarbocyanine (OTCC) at air-water and air-solid interfaces have been studied. A single type of domain and presumably of one single aggregate type has been found by Brewster Angle Microscopy. Peanut-shaped domains with internal anisotropy have been observed. However, this structure leads to a complex absorption spectrum which shows 4 bands, two red-shifted (822 nm and 757 nm), and two blue-shifted (600 nm and 530nm) with respect to the monomer band (665 nm). Our results confirm that all the absorption components are polarized in approximately the same direction. The absence of emission spectrum indicates that this interfacial aggregate cannot be classified as J-aggregates. Moreover, these bands cannot relate to Davydov splitting, given that all of them have the same polarization direction. We propose possible explanations based on a strong exciton-phonon interaction, and/or the formation of aggregates with different coherent lengths within the domain. The basic exciton model cannot explain this behavior. The coherent aggregate described in this study is proposed as a unique dye supramolecular structure obtained by assembly at the air-liquid interface.

2.1. Introduction

On elucidating how the structural details determine the optical properties, one can envision tuning the properties of materials by altering the molecular packing within the nanoscale structure of the assembly.¹ Since the 1930s, it has been known that by increasing the concentration of some cyanine dyes in an aqueous solution results in the observation of a new narrow, intense, and red-shifted absorption and emission band due to the formation of J-aggregates.²⁻³ The spectral properties of dye aggregates could be related to the molecular packing of the chromophores.^[3] Dye aggregates with a narrow absorption band that is shifted to a longer wavelength with respect to the monomer absorption band and a nearly resonant fluorescence, i.e., quite small Stokes shift, with a narrow band are generally termed J-aggregates. On the other hand, aggregates with absorption bands shifted to shorter wavelength with respect to the monomer band, are called H-aggregates and exhibit low or no fluorescence. The great significance of J-aggregates was recognized due to its optical and photophysical properties. Excellent monographs and reviews about J-aggregation are available in the literature.⁴⁻¹⁰

Cyanines can be aggregated in different ways depending on their structure and the medium (bulk solution or interface), resulting in aggregate modes that do not necessarily respond to simple J or H models. So, sometimes the monomer absorption band is splitted and two bands appear simultaneously shifted to higher and lower wavelengths than the monomer.¹¹⁻¹³ This behavior has been explained based on the formation of Davydov aggregates,¹⁴ i.e., aggregates in which the molecules adopt nonequivalent positions in the structure formed. According to Davydov's exciton theory, a given molecular energy level may be split into as many components as there are inequivalent molecules per unit cell. These aggregates are easily characterized because the different bands show different polarization properties.¹⁵

However, under certain experimental conditions, aggregates not fully adapting to the described models have been found. Thus, certain cyanine

derivatives form a double layer tubular strandin solution,¹⁶⁻¹⁸, being possible to observe as the absorption spectrum shows four bands in the visible region, three of them with the same polarization direction, while the fourth band shows a polarization perpendicular to the other.¹⁸ The interpretation of this behavior is complex, and the experimental results indicate that two of these bands are due to Davydov splitting, the third band has vibronic nature, while the fourth one is due to tubular segments of smaller delocalization length.¹⁸ An alternative explanation has been proposed where the tubular supramolecular model system is composed of two separate excitonic subsystems that are weakly coupled electronically.¹

In this paper the behavior of Langmuir monolayers of N'-dioctadecylthiapentacyanine (OTCC) has been described. Under certain experimental conditions, OTCC patterns a single type of domain and presumably of one single aggregate type, forming structures of the size of the order of micrometer. However, these structures lead to a complex absorption which shows four bands, as in the case of the tubular aggregates. Different studies show that all the bands are polarized in the same direction. The basic exciton model cannot explain this behavior. Some possible explanations based on a strong exciton-phonon interaction, and/or the formations of aggregates with different coherent lengths within the domain are proposed.

2.2. Results and Discussion

2.2.1. Surface pressure - Area isotherm

Figure 2.1 (solid line) shows the $\pi - A$ isotherm of the OTCC monolayer on a pure water subphase. The take-off of the isotherm occurs at $\sim 2.15 \text{ nm}^2/\text{molecule}$, with a phase transition at $\sim 5 \text{ mN/m}$. The monolayer collapse takes place at a surface pressure of $\sim 40 \text{ mN/m}$, and an area per molecule of ca. 0.8 nm^2 . The beginning of the phase transition takes place with an overshoot, see Figure 2.1. The overshoot takes place for all values of compression rate monolayers tested, even the slowest allowed by our experimental device, namely $0.04 \text{ nm}^2/\text{minute}^{-1}\text{molecule}^{-1}$. In this case, the

overshoot coordinates are ca. 4.8 mN/m and 1.9 nm² per molecule. The overshoot is a function of the monolayer compression rate. As is shown in Figure 2.1 (inset) when the compression rate is increasing, the overshoot is shifted to a higher surface pressure and a lower surface area.

Vollhardt and Retter defined the critical surface pressure, π_{crit} , as the minimum surface pressure required for the formation of nuclei.¹⁹ One reason for the appearance of the overshoot is because the nucleation process is, in any case, slower than the monolayer compression rate. To check this, some experiments were performed in which the monolayers were compressed at a slow compression rate until a surface pressure constant was reached at a previous point before the overshoot (see Inset Figure 2.1). In these experiments, the application of a surface pressure $\pi_{\text{constant}} < 4 \text{ mN/m}$ does not lead to the monolayer condensation (data not shown). On the other hand, when $\pi_{\text{constant}} \geq 4 \text{ mN/m}$, the monolayer begins to contract due to the feedback control system. In these cases the area relaxation is due to the nucleation and growth process at the monolayer. The Inset in Figure 2.1 shows the π - A recording when $\pi_{\text{constant}} = 4 \text{ mN/m}$. Therefore, $\pi_{\text{crit}} \approx 4 \text{ mN/m}$.

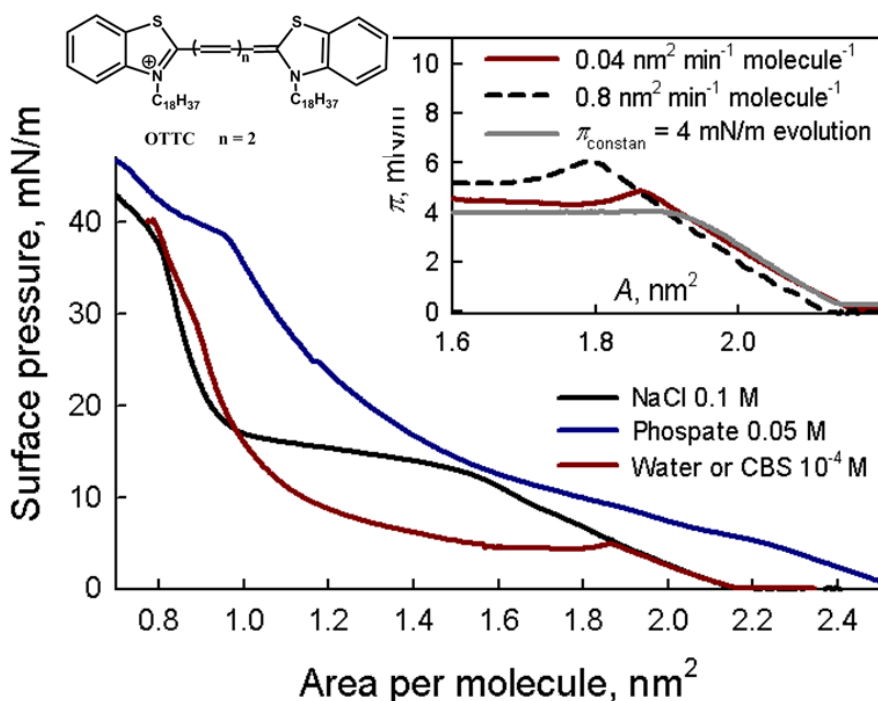


Figure 2.1: Surface pressure-area (π - A) isotherms of OTCC monolayer. Red line: Pure water subphase. Black line: 0.1 M NaCl subphase. Blue line: 0.05 M phosphate buffer subphase. Inset: π - A isotherms for different compression rates as specified within the graph and evolution of the monolayer at 4 mN/m. Top left, Molecular structure of OTCC.

The possible counterion influence on the monolayer formation has been studied. Figure 2.1 also shows the π - A isotherms for the OTCC monolayer using 0.1 M NaCl (Black line) and 0.05 M phosphate buffer (Blue line) as subphases. Additionally, no influence of a 10^{-4} M CBS as subphase was observed in the surface pressure-molecular area isotherm of OTCC. The π - A isotherm obtained in presence of NaCl resembles that one obtained at the aqueous subphase. The main differences are that the phase transition occurs at about 12-13 mN/m and that the overshoot is not observed. However, in the presence of phosphate buffer, the isotherm is quite different from the above. Thereby, the take-off of the isotherm occurs at ~ 2.5 nm²/molecule, two phase

transitions can be observed at $\sim 5\text{mN/m}$ and $\sim 38\text{mN/m}$ and finally, the collapse pressure slightly increases with respect to the previous cases.

For all tested subphases, the area per molecule near the collapse surface pressure was about 0.8 nm^2 per molecule. The length of the OTCC polar group (thiapentacarbocyanine, see Figure 2.1 for structure) is $\sim 1.94\text{ nm}$. This distance was calculated by optimizing the OTCC geometry using the semi-empirical PM3 method. Assuming a separation between polar groups of $\sim 0.4\text{ nm}$ at high surface pressure, the area occupied at the interface per polar group should have a minimum value of $\sim 0.78\text{ nm}^2$, which is close to the area found per OTCC molecule, i.e., $\sim 0.8\text{ nm}^2$. This coincidence suggests that neither the counter-ion, nor the alkyl chain, contribute to the net area occupied by the molecule at the interface, at least for high values of surface pressure.

2.2.2. Brewster Angle Microscopy (BAM)

Simultaneous to the isotherm recording, the morphology of the mixed monolayers was directly observed at the air-water interface by BAM. Figure 2.2 shows images corresponding to aqueous subphase, or with 10^{-4} M CBS in the suphase. Before the isotherm take off, honeycomb-like domains were observed (Figure 2.2a-b). Once the isotherm take off was reached the monolayer became homogeneous. The homogeneity persists until the overshoot was reached (Figure 2.2c).

After crossing the overshoot (Figure 2.2d), we could observe the appearance of elongated domains which evolved toward peanut or dog bone shapes. These peanut-like domains display inner anisotropy, such that its vertical regions were dark, while its horizontal ones were clear. The texture of the domains arises from the relative orientation of the dipoles with respect to the p-polarized laser incident. This phenomenon will be discussed in detail below. The domains grow as the surface pressure (Figure 2.2e) is increased until they completely cover the interface (Figure 2.2f). The domains do not coalesce when high surface pressures were applied.

The average size of the domains depends on the monolayer compression rate. For high compression rates, many small domains appear. Figure 2.2g shows an image obtained at a high surface pressure when the compression rate was $0.8 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$. By contrast, the domain number decreases but reaching larger sizes, as the compression rate is diminished (Figure 2.2f). Larger domains are obtained by applying a constant pressure of 4 mN/m allowing the monolayer to evolve with time, as described above (Inset of Figure 2.1).

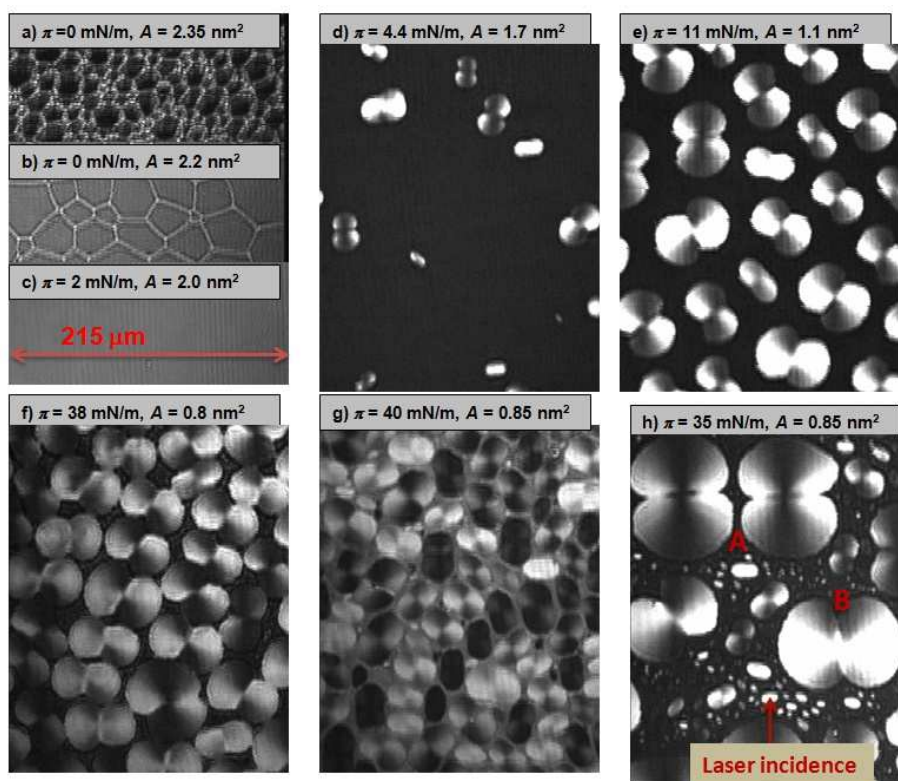


Figure 2.2: BAM images of the OTCC monolayer: a)-f) Images obtained along the compression process (compression rate $0.04 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$); g) Image obtained at high surface pressure when the compression rate was $0.8 \text{ nm}^2 \text{ min}^{-1} \text{ molecule}^{-1}$; h) Image obtained applying a constant pressure of 4 mN/m and leaving the monolayer to evolve with time, after a constant compression rate was re-applied up to high surface pressure.

The domains thus obtained are shown in Figure 2.2h. In the experiment corresponding to Figure 2.2h, after leaving the domains to grow, a

constant compression rate was re-applied upto high surface pressure. In this way we could appreciate the emergence of new domains of smaller sizes. In this selected figure 2.2h, we can observe three large domains, two vertically positioned with respect to the incident laser (A domains) and one positioned horizontally (B domain).

In all the images shown in Figure 2.2, the laser polarizer and analyzer were placed parallel (both in p position). In Figure 2.3a, an image in which the analyzer is rotated 90° with respect to the polarizer can be observed. Note that these domains show a striking texture that will be analyzed later. The decompression of the Langmuir monolayer leads to the complete disappearance of the domains, so in a second compression cycle a $\pi - A$ isotherm without appreciable hysteresis with respect to the first cycle (data not shown) is registered. However, a noteworthy phenomenon takes place during the early stages of decompression. Before the disappearance of the domains, each domain is divided into two breaks in its central region (see Figure 2.3b). Decompression results in the separation, probably because of the repulsion between the two broad side regions of the domains, which apparently were not united, but only through a narrow central region. This central region is the first to be broken when the monolayer is decompressed (see Figure 2.3b, bottom).

The monolayers can be transferred from the air-water interface to solid supports without a loss of organization. In Figure 2.3c, a BAM image of an OTCC monolayer transferred on quartz at the surface pressure of 9 mN/m by the LS method is displayed. The image clearly shows domains with the same shape as those observed at the air-water interface. In this image, the polarizer was disposed at 45° to increase the contrast. Therefore, the dark line that crosses domain is rotated 45° from the image vertical, which is coincident with the direction of the incident laser.

Figure 2.3d-e shows BAM images of the OTCC monolayers by using 0.1 M NaCl as subphase. The monolayer appears homogeneous before the phase transition. When the surface pressure is approximately 12 to 13 mN/m,

irregularly shaped domains begin to appear, some of which are bright and other dark (Figure 2.3d). The domains grow with branched shape as the surface pressure increases, so that the branches with grow parallel to the laser incidence axis are bright, while those grown perpendicularly are dark (Figure 2.3e).

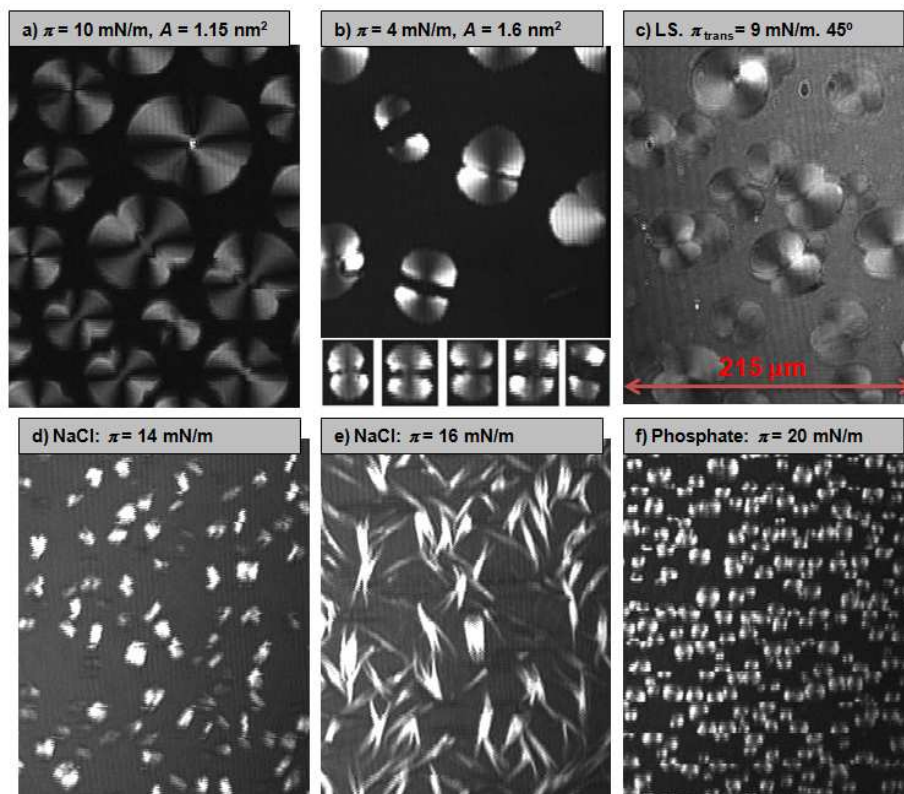


Figure 2.3: BAM images of the OTCC monolayer: a) analyzer rotated 90° with respect to the polarizer; b) during the monolayer decompression; c) an LS monolayer transferred on quartz. The transfer surface pressure was 9 mN/m , and the analyzer was rotated 45° ; d)- e) 0.1 M NaCl as subphase; f) $0.05 \text{ M phosphate buffer}$ as subphase.

Figure 2.3f shows BAM images of the OTCC monolayers by using $0.05 \text{ M phosphate buffer}$ as subphase. As for the previous case, the monolayer appears homogeneous before the first phase transition. At a surface pressure of $\sim 5 \text{ mN/m}$ small circular domains with internal anisotropy begin to appear.

The Polarization Modulated InfraRed Reflection Absorption Spectroscopy (PM-IRRAS) spectra of the OTCC monolayers at high surface pressure show absence of signal in the CH₂ region. That means the alkyl chains are in a quite low state of ordering. Therefore, the observed domains are exclusively caused by the aggregation of polar groups.

2.2.3 UV-Vis Reflection Spectroscopy (UVR) at the air-water interface.

The UV-vis reflection spectroscopy at the air/water interface allows obtaining in situ quantitative information on the presence and orientation of the chromophores at the interface. The UV-vis reflection spectroscopy is exclusively sensitive to the molecules existing at the air/water interface, therefore discarding any signal from the subphase. For a Langmuir monolayer containing UV-vis absorbing molecules, the reflection of light under normal incident at the interface is enhanced by:²⁰⁻²²

$$\Delta R_n = R_{D,S} - R_S = 2.303 \times 10^3 f_o \varepsilon \sqrt{R_S} \Gamma \quad (2.1)$$

where R_S and $R_{D,S}$ are the reflectivity of the interface with and without the presence of the Langmuir monolayer, respectively. $R_S \approx 0.02$, and ε is the molar absorption coefficient with mol·L⁻¹·cm⁻¹ units, Γ is the surface concentration of the monolayer, with mol·cm⁻² units, and f_0 is the orientation factor, which accounts for the change in the absorption properties of the chromophore due to anisotropy. Given a non-degenerated absorption band, that is, with only one component of the transition dipole, the orientation factor is:²²

$$f_0 = \frac{3}{2} \langle \cos^2(\theta) \rangle = \frac{3}{2} P(\theta) \quad (2.2)$$

where θ is the angle formed by the transition dipole and the normal axis to the air/water interface, and brackets indicate average values. $P(\theta)$ is also called the order parameter.²² Thus, a transition dipole orientation parallel with

respect to the interface implies that $f_0 = 1.5$ or $P(\theta) = 1$, whereas if the orientation is perpendicular, $f_0 = 0$ or $P(\theta) = 0$.

Figure 2.4 shows the UV-vis reflection spectra for the OTCC monolayer (water or 10^{-4} MCBS subphases) at different surface areas. As reference, the UV-vis absorption spectrum of the OTCC molecule in solution is also included (dotted line). The solution spectrum shows an intense band centered at 665 nm ($\epsilon_1 = 2.4 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$), due to the $0 \rightarrow 0$ transition and one vibronic sub-band at around 610 nm.¹² This vibronic structure can be attributed to certain essentially harmonic vibrations, largely to C-C valent vibrations in the $1300\text{-}1400 \text{ cm}^{-1}$ range.²³ In fact, the separation between the 665 nm and the 610 nm bands is 0.168 eV, which is equivalent to 1355 cm^{-1} .

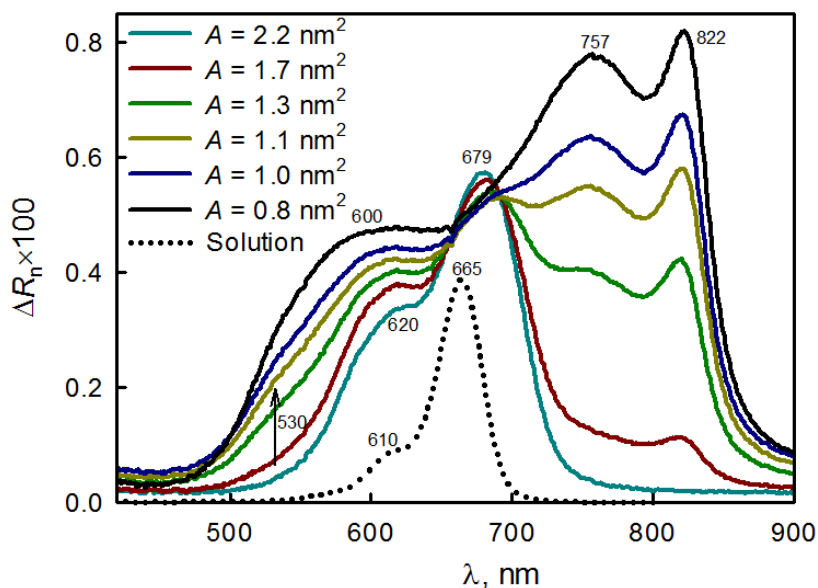


Figura 2.4: UV-vis reflection spectra of the OTCC monolayer (water subphase) at different surface areas. The UV-vis spectrum of OTCC in bulk solution (chloroform: methanol, ratio 3.1 (v/v)) is included for comparison (black dotted line).

Before the domain formation, the reflection spectrum show peaks centered at 679 and 620 (see Figure 2.4). In this case, the separation between the bands is 0.174 eV, which is equivalent to 1400 cm^{-1} . When domains began to appear, the above bands disappeared, while simultaneously new bands were observed at 822 nm, 757 nm, 600 nm and 530nm. The bands at 600 and 530 nm emerge at high surface pressure as a single broad band (see Figure 2.4).

UV-vis reflection spectra are often expressed in normalized units in order to discard any additional effect to the variation of the surface concentration of the chromophore at the interface. The surface concentration of the dye molecule is expressed by $\Gamma = 10^{14}/(N_A \cdot A)$, where N_A is the Avogadro number, and A is the OTCC molecular area. The normalized reflection signal is the product of the absolute reflection signal by the molecular area of the chromophore:

$$\Delta R_n^N = A \times \Delta R_n = \frac{2.303 \times 10^{17} f_0 \epsilon}{N_A} \sqrt{R_s} = 5.41 \times 10^{-8} f_0 \epsilon \quad (2.3)$$

ΔR_n^N has $\text{nm}^2 \cdot \text{molec}^{-1}$ units. The normalized reflection spectra offer information on molecular aggregation, as well as in molecular orientation. Figure 2.5 shows ΔR_n^N for the OTCC monolayer in presence of different ions in the subphase, at 38 mN/m.

Spectra obtained at high surface pressure, both on NaCl and phosphate subphases are very similar to those obtained on pure water subphase. Thus, in the presence of phosphate, bands at 816 nm, 754 nm and a broad band at 605 nm (Figure 2.5, dotted line) can be seen. Meanwhile, on NaCl subphase, the bands appear at 807 nm, 746 nm and 600 nm (Figure 2.5, dashed line), although in this case, a band at 696 nm, is also observed, possibly due to non-aggregated OTCC molecules.

From Figure 2.5 it can be inferred that the aggregation at the molecular level is very similar in the three cases analyzed, although the shape and size of the BAM domains are very different, suggesting that the number of coherently coupled molecules is much smaller than the aggregate size. The

counterion does not seem to be a determining factor in the type of coherent aggregate formed, although it seems to take an active role in the size and geometry of the resulting domain.

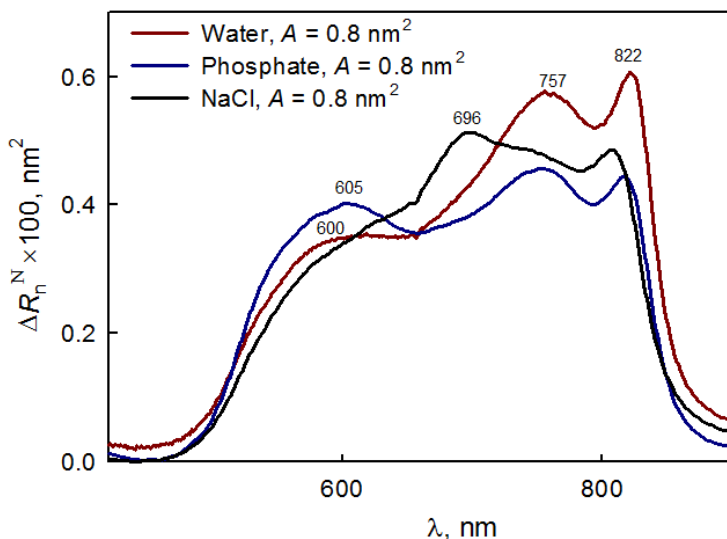


Figure 2.5: Normalized UV-vis reflection spectra of the OTCC monolayer obtained at 38 mN/m, $A = 0.8 \text{ nm}^2$ Red line: water subphase. Black line: 0.1 M NaCl as subphase. Blue line: 0.05 M phosphate buffer as subphase.

In solution, the intensity of an electronic absorption band is usually represented in terms of the so-called oscillator strength defined as:²⁴

$$f = \frac{4\epsilon_0 2.303 m_e c_0}{N_A e^2} \int_{\text{Band}} \epsilon d\nu = 1.44 \times 10^{-19} \int_{\text{Band}} \epsilon d\nu \quad (2.4)$$

where ϵ_0 is the permittivity of vacuum, m_e the electron mass, e the elementary charge, and c_0 the speed of light in a vacuum. The numerical factor 1.44×10^{-19} has units of $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm} \cdot \text{s}$. From equations 2.3 and 2.4, it is possible to define an apparent oscillator strength, f_{ap} , determined from the measured reflection spectra as

$$f_{ap} = f \times f_0 = \frac{3}{2} \times f \times P(\theta) = 2.6 \times 10^{-12} \int_{\text{Band}} \Delta R_n^N d\nu \quad (2.5)$$

where the numeric factor 2.6×10^{-12} is expressed in $\text{nm}^{-2}\cdot\text{s}$. Note that in the above definition, f is the oscillator strength in solution, i.e., isotropic conditions.

According to the Davydov model corresponding to excited states of weakly interacting molecules, oscillator strength is preserved in different aggregation state.^{4,14-15,24} In such a case, the variations of f_{ap} provide a direct measurement of the order parameter of the chromophores at the air/water interface. In solution we obtain the oscillator strength, $f \approx 1.5$ (integration from 500 nm to 750 nm), while at the air-water interface, $f_{ap} \approx 2.3$ (integration from 450 nm to 950 nm) is calculate, which is independent both of the salt used in the aqueous subphase and the surface pressure. Therefore, $f_0 \approx 1.5$ or $P(\theta) \approx 1$. Note that these values refer to the set of transitions observed in the visible. However, since $f_0 = 1.5$ is the maximum allowed value, this indicates that all the absorption components should be located parallel to the interface plane.

On pure water subphase and high surface pressures, the monolayer is coated with a single type of domain, and presumably one single aggregate type. However, the structure of the absorption bands is complex (see Figures 2.4 and 2.5). One possible explanation for this phenomenon is the existence of inequivalent molecules in the aggregate, i.e., the so-called Davidov's aggregate. According to Davidov's exciton theory, a given molecular energy level may be split into as many components as there are inequivalent molecules per unit cell.¹⁴⁻¹⁵ In addition to the spectral splitting, the Davydov bands must exhibit distinct polarization properties. However, the preliminary calculation performed above, indicates that all component transition dipoles are in the interface plane. The confirmation of this fact must be performed to obtain the polarization properties of each one of the absorption bands.

2.2.4 Polarization study of the absorption bands: out-plane anisotropy.

An *in situ* measurement of the orientation of the various absorption dipole components can be performed using UV-Visible reflection spectroscopy under variable angle incidence at the air-water interface with s- and p- polarized light.²² This technique has been recently developed, and depending on the incidence angle and the orientation of dipole absorption produces positive or negative bands when p-polarized radiation is used as absorption-reflection IR spectroscopy techniques. This technique has proven to be highly sensitive to resolve bands with different polarization.

In Figure 2.6, some spectra obtained from the OTCC monolayer (pure water subphase) at the surface pressure of 38 mN/m are shown. These spectra correspond to different incidence angles by using p- and s-radiation, also, for comparison the spectrum obtained at normal incidence of unpolarized radiation is shown (n-, Figure 2.6 black line). The relative height of the bands is approximately constant regardless of the angle of incidence and type p- or s-radiation used. This behavior is indicative that all the absorption components have the same average orientation with respect to the interface plane, approximately.

By fitting data to the Fresnel model corresponding to an anisotropic uniaxial film between two isotropic media (air and water), the $P(\theta)$ values for the different absorption components (822 nm, 757 nm and 600 nm) were obtained. Details on the procedure and fitting data can be found in the Supporting Information. In every case $P(\theta) \approx 0.9 - 1.0 \pm 0.1$ were obtained, which means a parallel orientation regarding to the interface.

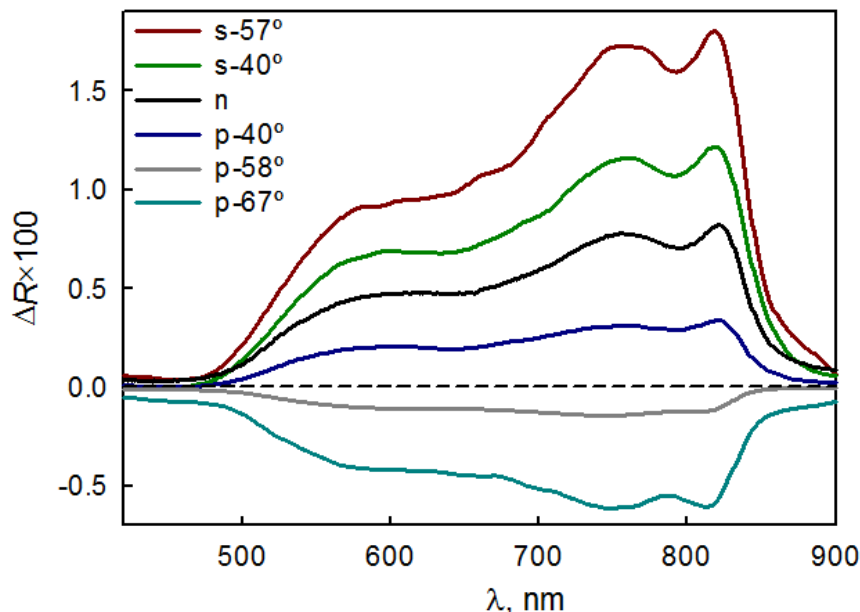


Figure 2.6: Reflection spectra, ΔR , of the OTCC Langmuir monolayer at different incidence angles for $\pi = 38$ mN/m. The incidence angle and the s-, or p-polarization are indicated in the figure. The n line corresponds to the spectrum obtained under unpolarized light and normal incidence.

Furthermore, the dichroic ratio measurements of the LS films of the OTCC transferred on quartz were done. This dichroic ratio was obtained from the ratio between the s- and p-polarized transmission spectra being 45° the incidence angle with respect to the air-solid interface. For all measurements the dichroic ratio was kept constant, and equal to about 1.5, in the region of the analyzed spectrum (500nm to 840nm). This dichroic ratio value is indicative of a parallel orientation with respect to the interface. Details are provided in the Supporting Information.

The conclusion both from Figure 2.6 and the dichroic ratio of the LS films has been obtained assuming that the films are isotropic in the plane, which is not strictly true due to the anisotropic character of the domains observed by BAM. However, when reflection or transmission spectrum is performed, the optical section is much larger than the domain size, so it can

be assumed that there are a lot of domains randomly oriented in that section, and therefore the film is isotropic in the plane as an average.

Our results confirm that the different absorption components are polarized in the plane of the interface. However, the experimental values of $P(\theta)$ have an estimated error of ± 0.1 , so small deviations out of the plane cannot be ruled out. Moreover, as shown above, the BAM images show a single domain type, which shows internal anisotropy (anisotropy in the plane). Understanding this phenomenon, allows us to check whether the different absorption components are polarized or not, in the same direction in the interface plane.

2.2.5 The origin of the domain anisotropy observed by BAM: in-plane anisotropy.

In standard BAM experiment, p-polarized light reaches the air-water interface with an angle of 53.15° (Brewster angle). The different BAM textures are usually observed due to changes of the refractive index resulting from differences in thickness, density and/or molecular orientation between the different regions of film. However, in the case of OTCC Langmuir monolayers, the OTCC aggregates absorb at the wavelength of 532 nm laser beam (see Figure 2.4). As previously established, the absorption originates the strong changes in the film refractivity, being this phenomenon mainly responsible for the appearance of domain textures. In such a case, the Fresnel equations for biaxial anisotropic materials on isotropic substrate should be used to calculate the reflection of the film.²⁵

In Scheme 1A some domains with different tilt degrees with respect to the vertical axis are shown, on which it is possible appreciate how the texture is changed as the domain tilt occurs. The vertical x axis (laboratory coordinates) is coincident with the projection of the laser incidence axis on the air-water interface. Scheme 1B shows the polar headgroup of the OTCC molecule. In this Scheme 1B, μ (red arrow) is defined as the main thiapentacarbocyanine transition dipole which is located parallel to the

interface (x-y plane). We assume that the transition dipole is rotated an angle ϕ with respect to the x axis (Scheme 1B).

The inner textures of the domains can be simulated disregarding the presence of the alkyl chains. Thus, the monolayer is considered as a biaxial materials with the complex refractive indices of $N_q = n_q - ik_q$ ($q \equiv x, y$ and z), where n_q is the real part of the refractive index, and k_q is the absorption coefficient of the monolayer (see details in the Supporting Information).²⁵ The BAM images shown in Scheme 1C were recorded with the camera polarizer (analyzer) at 0° . This polarization angle implies that only the p component of the reflected radiation is detected. If, as obtained previously, it is assumed $\theta \approx 90^\circ$, only the k_x component plays a role in the acquired BAM pictures. In such a case, it may be demonstrated that the reflection near the Brewster angle is approximately proportional to $\cos(\phi)^4$ (see Supporting Information). However, reflection quantification requires Fresnel equations. Therefore, the different textures of the domains are due to the different orientations of the polar group with respect to the incident laser.

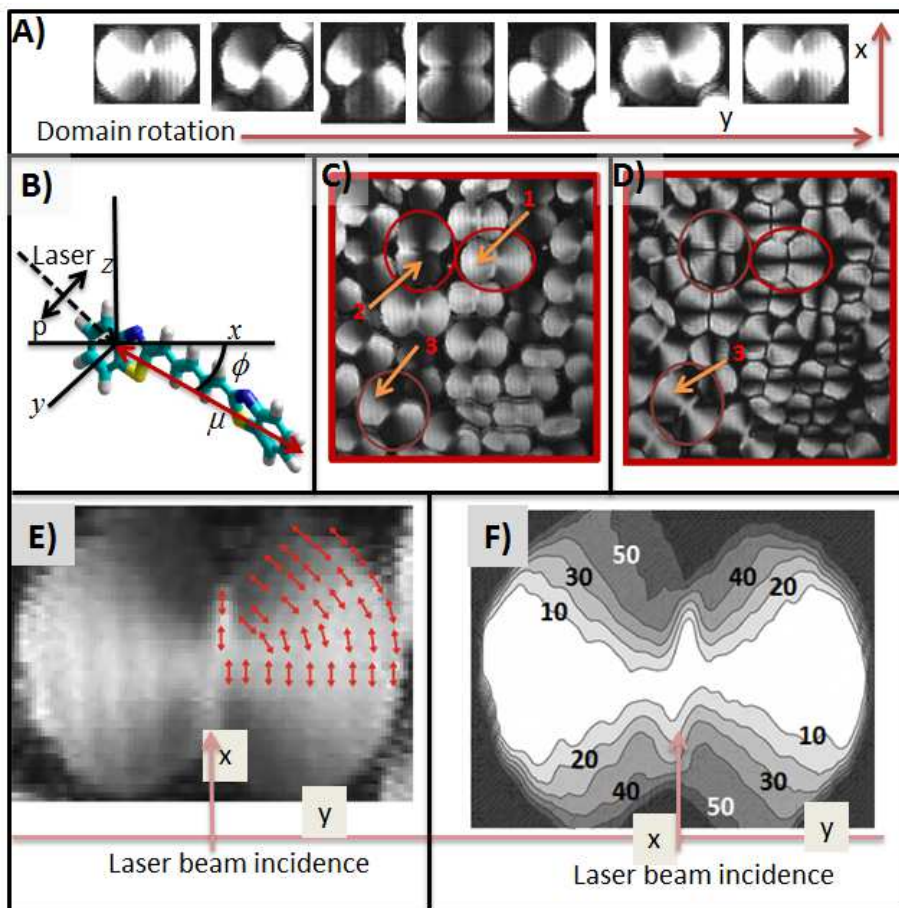
By using this simple model it is possible to determine the transition dipole orientation (ϕ angle) in each domain region based on its reflectivity. On this basis, it is assumed that the intensity of each pixel of BAM image (0-255 grayscale) is proportional to the reflectivity. However, the pixel intensity is a relative magnitude dependent on the exposure time. To establish a quantitative relationship between reflectivity and grayscale, BAM pictures not saturated by high or low intensity, i.e. images where neither zero nor 255 in gray scale were reached (images shown in Figure 2.2e and 2h are saturated by high intensity) are required. An unsaturated image is shown in Scheme 1C. In this image, three domains have been selected (marked with red circles), as reference domains, for which $\phi = 0^\circ$ for the brightest regions (point 1 in Scheme 1C) and $\phi = 90^\circ$ for the darkest one (points 2 in Scheme 1C) have been set.

The quantitative relationship between reflectivity and gray scale can be completed with the image shown in Scheme 1D. This image shows the same domains which may be observed in Scheme 1C, although now the BAM analyzer was rotated at 90° with respect to the polarizer. In this case, the incident radiation is p polarized, but only the s component of the reflected radiation is detected. Under these experimental conditions, k_x and k_y components of the absorption coefficients contribute to the reflectivity. The reflectivity should be proportional to $\cos(\phi)^4 \times \sin(\phi)^4$. This function has a maximum for $\phi = 45^\circ$, therefore the brightest regions of the domains in the Scheme 1D should correspond to this rotation angle of the transition dipole and point 3 in Schemes 1C and 1D should be associated with a value $\phi = 45^\circ$. Note that the $\cos(\phi)^4 \times \sin(\phi)^4$ function has minima for $\phi = 0^\circ$ and $\phi = 90^\circ$ corresponding to the domain darkest regions in Scheme 1D.

In Scheme 1E a horizontally oriented domain is shown, i.e., along the y axis. The size of this domain is about $60 \mu\text{m}$ long by $40 \mu\text{m}$ wide. Inside this domain the progressive rotation of the transition dipoles are represented in a sketchy way with red arrows. In the Scheme 1F, the ϕ values are shown as contours. These ϕ values were calculated for the previous domain and by using a linear relationship between the pixel intensity and the function $\cos(\phi)^4$. In the graph, the labels mark regions within which the angle ϕ is less or equal than the value indicated.

As deduced from the foregoing the anisotropy observed in the BAM domains is due to the different orientations between the molecule transition dipole and the laser incidence axis (x axis, see Scheme 1B). However, all BAM images shown in Figure 2.2 and 2.3, and in Scheme 1, have been taken using a 532 nm laser, so that all the previous arguments refer exclusively to this absorption component. It has been shown that all aggregate absorption components are polarized in the interface plane, approximately, although it is possible that these components could have a different orientation inside the plane. By using a laser with different wavelength can result in different

domain textures if indeed absorption modes have different in-plane polarizations.



SCHEME 2.1: A) Some domains with different tilt degrees with respect to the vertical axis. B) Polar headgroup of the OTCC molecule. The red arrow represent the main transition dipole, μ , and ϕ is the angle between μ and the x axis. C) BAM images of the OTCC monolayer obtained at 38 mN/m. D) This image shows the same domains that in C, although now the BAM analyzer was located 90° with respect to the polarizer. E) Domain in which the progressive rotation of the transition dipoles are represented in a sketchy way with red arrows. F) The ϕ values are shown as contours inside a domain.

Additionally, BAM images using a 658 nm laser have been recorded. Figure 2.7A shows an image of the monolayer at $\pi = 20$ mN/m. As can be seen, the domain textures are identical to those obtained at 532 nm. Moreover, BAM images have been obtained by using monochromatic light sources at 780 nm and 810 nm from a xenon lamp with a monochromator. In these cases the power of the lamp is much lower than the lasers and the images are less clear-cut. Besides, in this wave, only a narrow region BAM display (frame) has only been able to get in focus. Figures 2.7B and 2.7C show images obtained at 780 and 810 nm, respectively. As can be seen the texture of the domain is the same that in the previous case, leading us to conclude that all the absorption components are polarized in the same direction inside the interface plane.

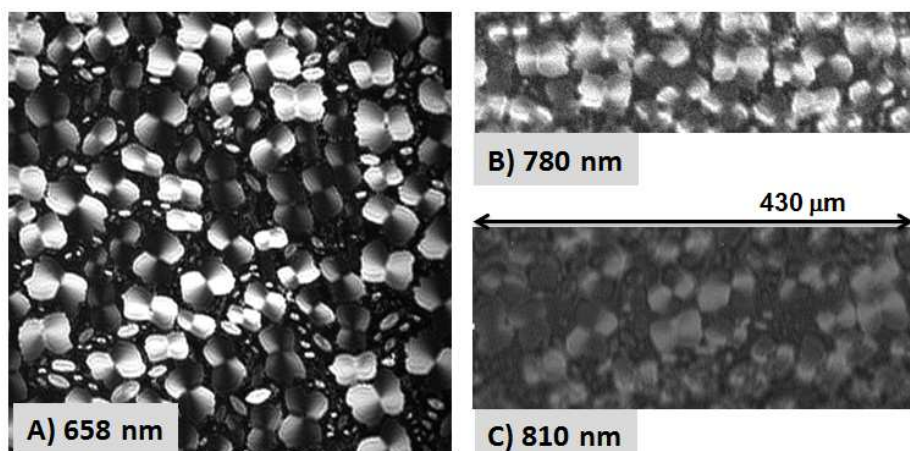


Figure 2.7: BAM images of the OTCC monolayer at $\pi = 20$ mN/m under: A) 658 nm laser; B) 780 nm monochromatic light; C) 810 nm monochromatic light.

In view of the results shown above, it can be deduced that the OTCC molecules exhibit a striking aggregation pattern forming peanut shaped domains. These domains can be described with two axes: a) short axis, in the narrowest part of the domain, which coincides with the x axis in the domains shown in Schemes 1D and 1F; b) long axis, which coincides with the y axis in these schemes.

Furthermore, two regions can be distinguished within the domain, in which the aggregation of cyanine appears to be different. The first one is the narrow central region extended along the short axis of the domain, where the polar group is located parallel to such axis, and there is no apparent rotation of a molecule relative to another. The second one is the two wide lateral regions in which the cyanine dye is aggregate in a fan shape. In this latter case, the cyanine groups rotate slightly as they shift away from the long axis, but such rotation is always less than 90° respect to such axis. Such rotation is indicative of the chiral aggregate formation, although, and since there are molecules that rotate in both directions in the same domain, the domains must be achiral, as it has been verified experimentally.

2.2.6 Energy transfer from an Ir complex to OTCC on quartz.

The OTCC molecule possesses a high fluorescence quantum field in solution (chloroform/methanol) with an intense emission band centered at 710 nm assigned to the OTCC monomer. However, no fluorescence signal was detected in the OTCC monolayers transferred from the air-water interface to the quartz substrates. Different transfer conditions were probed, i.e. a variety of surface pressures and deposition of mono or multilayers, always with the same result. The same behavior has been reported previously in monolayers of the same cyanine but with $n = 0$ and $n = 1$ (see Figure 2.1), which is attributed to the fast non-radiative deactivation pathways occurring in the aggregates.^{11,26} In line with this, in mixed films containing the cyanine derivative with $n = 1$ and stearic acid, fluorescence signal was detected, which was assigned to the disaggregation effect of the stearic acid in the cyanine molecules.²⁶

However, despite the absence of fluorescence emission of the OTCC layers, the molecular photonics properties of the aggregates can be exploited. Thus, to investigate potential photophysical reactions in the OTCC layers, monolayers of a cationic iridium complex mixed with an anionic phospholipid

(1:1) were deposited together with the OTCC layers, fabricating different systems by alternative deposition of the monolayers. First, a LS monolayer of the iridium (Ir) complex was transferred on top of the quartz substrate. Then, a variable number of monolayers of arachidic acid were deposited by using the LB method. Finally, a LS monolayer of the OTCC molecule was transferred and the complete system can be named as Ir complex/AA_x/OTCC, with x representing the number of transferred monolayers of the arachidic acid.

The complete system is irradiated with monochromatic light at 300 nm to selectively excite the Ir complex since the OTCC aggregates do not absorb at this wavelength. In case $x = 5$, or when the OTCC monolayer is not transferred, a strong fluorescence signal is registered, which corresponds to the Ir complex emission band (red line in Figure 2.8).²⁷ Thus, no interaction between the Ir complex and the OTCC aggregates takes place at long separation. If $x = 1$, the emission band drops to about half of the previous value, but keeping the same shape (blue line in Figure 2.8). Finally, if $x = 0$, almost no emission is detected (black line in Figure 2.8). Thus, the quenching of the fluorescence emission of the Ir complex is more intense when the OTCC monolayer is closer to the Ir complex layer. We believe that this distance-dependent quenching of the Ir complex emission is caused by a Förster-type energy transfer process, which is feasible to the good overlap between the emission spectra of the iridium complex and the absorption band of the cyanine aggregates. This energy-transfer reaction together with the broad and infrared-shifted absorption spectrum of the OTCC aggregates prove that these films might be integrated in molecular electronic devices, as light emitting diodes or solar cells.

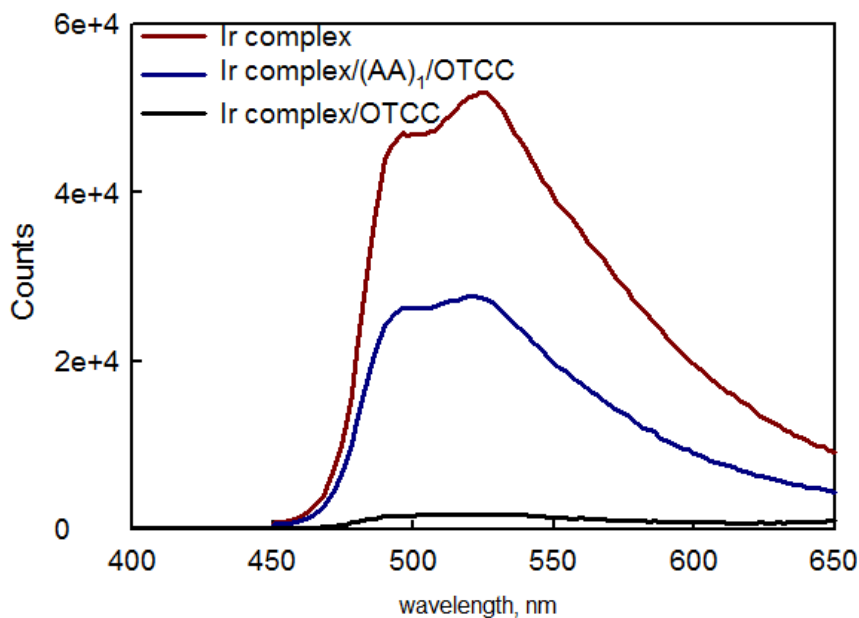


Figure 2.8: Emission spectra of an Ir complex monolayer (red line), Ir complex/AA/OTCC multilayer (blue line) and Ir complex/OTCC multilayer (black line). $\lambda_{\text{exc}} = 300 \text{ nm}$.

2.3. Conclusion

Langmuir monolayers of OTCC at the air-water and air-solid interfaces have been studied. We have found that the π - A isotherms and the domains observed by BAM dependent on the counterion which is added to the aqueous subphase. In the presence of CBS as counterion, the BAM image shows the formation of a single type of domain and presumably of one single aggregate type. These domains are peanut shaped and have internal anisotropy, such that its vertical regions are dark, while its horizontal ones are clear. The texture of the domain is the result of its relative orientation with respect to the p-polarized laser incident. However, these singles structures lead to a complex absorption which shows 4 bands, at 822 nm, 757 nm, 600 nm and 530nm, although the bands at 600 and 530 nm appears at high surface pressure as a single broad band.

Spectra obtained at high surface pressure, in the presence of NaCl or phosphate subphase show very similar structures to those obtained when using CBS. The aggregation of the cyanine moiety at the molecular level is very similar in the three studied cases (number of coherently coupled molecules), although the shape and size of the BAM domains are very different. The counterion does not seem to be a determining factor in the type of coherent aggregate formed, although it seems to take an active role in the size and geometry of the resulting domain.

To determine the polarization of the different absorption bands we have performed “in situ” measurements by using UV-Visible reflection spectroscopy under variable angle incidence at the air-water interface with s- and p- polarized light. Moreover, we have determined the dichroic ration of the LS films. Our results confirm that the different absorption components are polarized in the plane of the interface. However, the experimental values of $P(\theta)$ have an estimated error of ± 0.1 , so that small deviations out of the plane cannot be ruled out.

In our BAM experiment, the OTCC aggregates absorbed at the wavelength of the microscope laser. As previously described,²⁵ the absorption originates strong changes in the film refractivity, being this phenomenon mainly responsible for the appearance of domain textures in BAM. In fact, the anisotropy observed in the BAM domains is due to the different orientations between the molecule transition dipole and the laser incidence axis (x axis, see Scheme 1B). In this way, the transition dipole orientation (ϕ angle) in each domain region can be determined based on its reflectivity through a quantitative relationship between reflectivity and the intensity of each pixel of BAM image. This fact opens a way to determine the polarization of each absorption component in the plane of the interface.

The use of BAM with monochromatic light sources at the wavelengths corresponding to the different absorption modes could result in different domain textures if indeed absorption modes have different in-plane polarizations. However, the use of monochromatic light sources at 660 nm,

780 nm and 810 nm allows us to observe BAM domains which have the same texture as described by using 532 nm (see Figure 2.2), which lead us to conclude that all the absorption components are polarized in the same direction, approximately.

In brief, by using pure water or CBS subphase, the OTCC molecules form a single type of aggregate at the air-water interface. However, this aggregate leads to 4 absorption bands in the visible region, two red-shifted ones, and two blue-shifted ones, with respect to the monomer band. The absence of emission spectrum indicates that this aggregate cannot be classified as J-aggregates. Also, these bands cannot relate to Davydov splittings, since all them have the same polarization direction.

There are some analogies between the behavior described and the behavior observed for certain cyanine derivatives which form double layer tubular strands in solution.^{16-18 21} Thus, the absorption spectrum shows 4 bands in the visible region, as in our case. However, unlike our system, 3 of the bands have the same polarization direction, while the fourth one shows a polarization perpendicular to the other.^{18 21} Another important difference is that these tubular structures are fluorescent. In any case, we note that the basic exciton model cannot explain three transitions oriented parallel and one perpendicular to the tubular axis, in the same way that this model cannot explain four transitions oriented in the same direction.

We believe that some of the bands observed for the OTCC monolayers may be due to the exciton-phonon interaction. This type of interaction is quite different for J or H aggregates. Thus, for J aggregates, the vibrational structure tends to decrease when the number of the coherently coupled molecules increases. While for H aggregates, the vibrational structure is enhanced, and several bands of this type may appear.^{10,23,28-29} Thus, a possibly partial explanation of the complex absorption of our system could be the formation H-aggregate with a strong exciton-phonon interaction. However, a drawback of this interpretation is that we can hardly classify our aggregate as a H-aggregate, because there are two red-shifted and two blue-

shifted absorption bands, with respect to the monomer band, being the most intense the red-shifted one, but, as was indicated above, our aggregate cannot be classified as a J-aggregate either, due to the emission absence.

The definition of the H or J aggregate is performed in function of the blue-shift (H), or red-shift (J) absorption band displacement respect to the non-aggregated specie band. However, in our case the position of the non-aggregated specie band could not be well defined. The OTCC molecule have two benzothiazole groups (aromatic heterocyclic), which have flat structures. However, these two groups are not coplanar with each other due to steric hindrance. We have performed an optimization of the geometry of this molecule using the PM3 semi-empirical method, obtaining an angle between such planes of $\sim 26^\circ$. Also, we have optimized the geometry of the OTCC dimer and tetramer. CBS molecules have been added to these OTCC structures to compensate the charge and prevent electrostatic repulsion between OTCC molecules. For these aggregated forms, it has been found that the angle between the benzothiazole planes decreases to $\sim 15^\circ$ - 20° . This phenomenon has a considerable influence on the position of the absorption band in aggregation absence, because when the angle between planes decreases, the conjugation with the double bonds of the chain increases, and therefore the band shifts to the red. Thus the red-shift may not be due exclusively to the J aggregate formation, but due to this other phenomenon, that is, the conjugation increase.

An alternative explanation not excluding the previous discussion could be the formation of aggregates with different coherent lengths within the domain. As commented, two regions can be distinguished within the domain, in which the aggregation of cyanine appears to be different. The first is the narrow central region, where there is no apparent rotation of the polar group relative to another and the second is the two wide lateral regions in which the cyanine dye is aggregate in a fan shape, and there is rotation with respect to other cyanine groups. The disadvantage of this idea is that the same

absorption bands can be observed in the presence of NaCl or phosphate subphase although the shape and size of the BAM domains are quite different.

2.4. Experimental Section

Materials: The salt of the dye cationic N,N'-dioctadecylthiapentacarbocyanine (OTCC) with anionic 4-chlorobenzenesulfonate (CBS) as counterion was synthesized by J. Sondermann at the Max-Planck-Institut für biophysikalische Chemie.³⁰ A mixture of chloroform:methanol, ratio 3:1 (v/v), was used as the spreading solvent for dissolving OTCC. The Ir-dye complex [Ir(ppy)2(tmphen)]PF₆, being tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, and ppy = 2-phenylpyridine, was synthesized as previously described.²⁷ Dimyristoyl-phosphatidic acid (DMPA) and arachidic acid (AA) were purchased from Sigma Chemical Co. and used as received.

The pure solvents were obtained without purification from Aldrich. Potassium Phosphate, NaCl and sodium 4-chlorobenzenesulfonate salts were purchased from Sigma-Aldrich. Ultrapure water, produced by a Millipore Milli-Q unit, pretreated by a Millipore reverse osmosis system (>18.2 MΩ/cm), was used as a subphase. The subphase temperature was 21 °C with pH 5.7. For buffer solutions, the pH was adjusted to pH = 7.0 by adding dropwise a solution of NaOH 1M. The quartz substrates used were cleaned as follows: successive steps with an alkaline detergent, isopropanol, and ethanol and then thoroughly rinsed with ultrapure water.

Methods: A NIMA 601 trough (Nima Technology, Coventry, England) equipped with two symmetrical barriers to record BAM images was used. Images of the film morphology were obtained by Brewster angle microscopy (BAM) with a I-Elli2000 (Accurion GmbH, Göttingen, Germany) using a Nd:YAG diode laser with wavelength 532 nm and 50 mW. Lateral resolution of the BAM microscope is 2 μm. The image processing procedure included a geometrical correction of the image, as well as a filtering operation to reduce interference fringes and noise, with no additional treatment. No

optical filters were applied during the BAM experiments. Polarizer and analyzer were set at 0° (p-configuration), unless it is expressly stated. The microscope and the film balance were located on a table with vibration isolation (antivibration system MOD-2 S, Accurion GmbH, Göttingen, Germany) in a large class 100 clean room. Additionally, some BAM images have been obtained by using a SIENep3se in the Accurion Labs (Göttingen, Germany), with a xenon plus arc lamp with a monochromator as light source which permits to obtain images at different wavelengths.

UV-visible reflection spectra under normal and variable angle incidence were obtained with a Nanofilm Surface Analysis Spectrometers: Ref SPEC2 at normal incidence and RefSpec2VA at variable angle incidence (supplied by Accurion GmbH, Göttingen, Germany).

UV-visible electronic absorption spectra of the films were measured locating the substrate directly in the light path on a Cary 100 Bio UV-visible spectrophotometer. The steady state fluorescence and excitation spectra were measured using a FS920 Steady State Fluorimeter (EdinburghInstrument, Livingston, UK). The excitation was at 274 nm.

The monolayers at the solid substrates were transferred at a constant surface pressure by the Langmuir–Schaefer (LS) technique, i.e., by horizontal touching of the substrate or by the Langmuir–Blodgett (LB) technique, i.e., by vertical dipping with a lifting speed of 5 mm×min⁻¹. For fluorescence measurements, the multilayers were assembled by the following sequence of monolayers: (1) one Ir complex/DMPA (1:1) monolayer transferred at 35 mN/m by the LS method; (2) 0, 1, 3 or 5 AA monolayers transferred at 25 mN/m by the LB method; and (3) one OTCC monolayer at 35 mN/m transferred by the LS method. The ratio of the transfer processes onto solid substrates was close to unity in all cases.

Acknowledgment

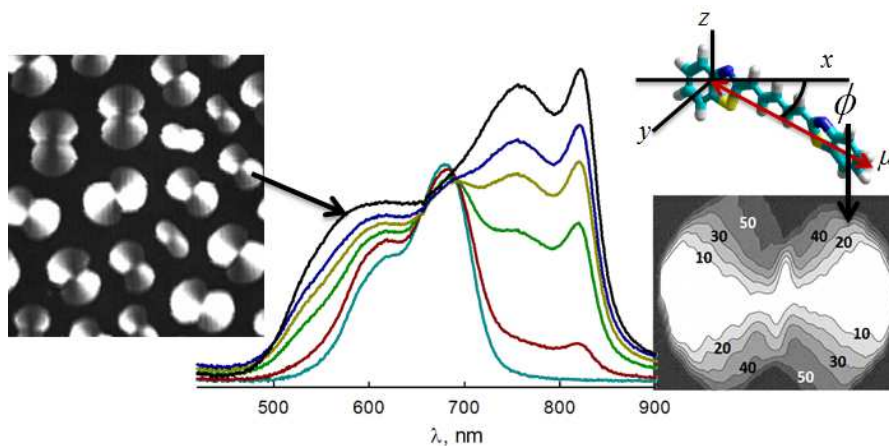
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Graphical abstract

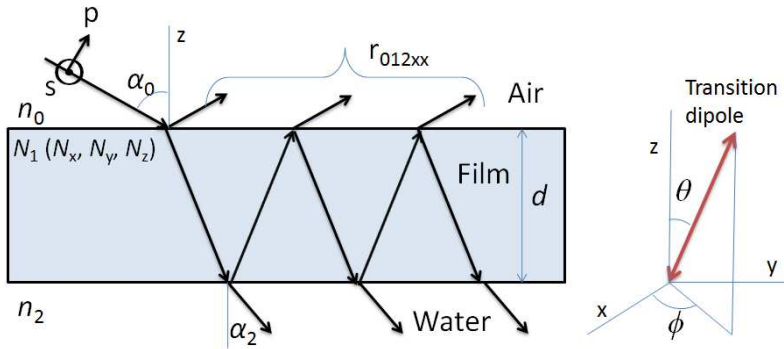


Exciton-phonon interaction: Coherent aggregates of a surface active organic dye containing a cyanine group self-assemble at air/liquid interface. The aggregates yields an unprecedented behaviour not predicted by the commonly used exciton model. On the other hand, the effective exciton-phonon interaction is found herein. This interfacial assembly is proposed as the first experimental example for a new series of dye aggregates with remarkable photophysical features.

2.5. Supporting Information

2.5.1. Anisotropic thin film on isotropic substrate

The anisotropic thin film is described with the complex refractive indices of N_x, N_y, N_z . As shown in Scheme SI.2.1, the reflection incidence angle α_0 and transmission angle α_2 of multiply reflected waves are constants and are related by $n_0 \sin(\alpha_0) = n_2 \sin(\alpha_2)$. $n_0 = 1$ (air) and $n_2 = 1.333$ (water) represent the real refractive indices of the ambient and substrate, respectively.



Scheme SI.2.1: Schematic illustration of reflection at a three-layer system in which layer 0, 1 and 2 represent is air, the thin film, and the subphase (water in this case). Left: Black arrows represent the incident light. Right: Red arrow represents the transition dipole direction, and x-y represent the interface plane.

The Fresnel expressions for the reflection of s- and p- polarized radiation under different α_0 originated for a anisotropy biaxial film between two isotropic media, e g., air and water are provided by:^[1]

$$r_{01pp} = \frac{N_x N_z \cos(\alpha_0) - n_0 \left(N_z^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}}{N_x N_z \cos(\alpha_0) + n_0 \left(N_z^2 - n_0^2 \sin(\alpha_0)^2 \right)^{1/2}}$$

$$r_{12pp} = \frac{n_2 \left(N_z^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} - N_x N_z \cos(\alpha_2)}{n_2 \left(N_z^2 - n_2^2 \sin(\alpha_2)^2 \right)^{1/2} + N_x N_z \cos(\alpha_2)}$$

$$r_{01ss} = \frac{n_0 \cos(\alpha_0) - \left(N_y^2 - n_0^2 \sin(\alpha_0)^2\right)^{1/2}}{n_0 \cos(\alpha_0) + \left(N_y^2 - n_0^2 \sin(\alpha_0)^2\right)^{1/2}}$$

$$r_{12ss} = \frac{\left(N_y^2 - n_2^2 \sin(\alpha_2)^2\right)^{1/2} - n_2 \cos(\alpha_2)}{\left(N_y^2 - n_2^2 \sin(\alpha_2)^2\right)^{1/2} + n_2 \cos(\alpha_2)}$$

The total reflection coefficients

$$r_{012xx} = \frac{r_{01xx} + r_{12xx} \exp(-2 \cdot i \cdot \beta_x)}{1 + r_{01xx} r_{12xx} \exp(-2 \cdot i \beta_x)}$$

Where x = s or p and

$$\beta_p = \frac{2\pi d}{\lambda} \frac{N_x}{N_z} \left(N_z^2 - n_0^2 \sin(\alpha_0)^2\right)^{1/2}$$

$$\beta_s = \frac{2\pi d}{\lambda} \left(N_y^2 - n_0^2 \sin(\alpha_0)^2\right)^{1/2}$$

Where λ is the wavelength and d is the thickness of the thin film. We obtain the reflected amount of light for x = s or p-polarized waves as follows:

$$R_x = |r_{012xx}|^2$$

The complex refractive indices of anisotropic materials along the x, y, and z axes are given $N_q = n_q - i k_q$, where, $q \equiv x, y, z$, being n_q the real part of the reflective index and k_q the absorption constant along each axes. The variations in reflection are assumed to be caused mainly by absorption, and $n_x = n_y = n_z = n_1$ can be assumed. Furthermore, the absorption constants can write as:

$$\begin{aligned} k_x &= 3k_{iso} \langle \sin(\theta)^2 \rangle \langle \cos(\phi)^2 \rangle \\ k_y &= 3k_{iso} \langle \sin(\theta)^2 \rangle \langle \sin(\phi)^2 \rangle \\ k_z &= 3k_{iso} \langle \cos(\theta)^2 \rangle \end{aligned} \tag{SI-2.1}$$

Where the brackets indicate average values, k_{iso} is the absorption constant in an isotropic media, θ is the angle between the normal to the air-water interface (z axis) and the direction of the transition dipole, and θ is the angle between the projection of the transition dipole on the xy plane and the x axis, see Scheme SI.2.1(right).

2.5.1.1. Polarization study of the absorption bands by using UV-Vis Reflection Spectroscopy under variable angle incidence.

The Fresnel expressions for the reflection of s- and p- polarized radiation under different α_0 can be used for obtaining the variation between the reflection of incoming radiation in presence and in absence of a Langmuir monolayer, ΔR .^[2] For uniaxial materials, and assuming that the film is isotropic in the plane as an average, it is possible to rewrite the equations (SI.2.1) as.

$$\begin{aligned} k_x = k_y &= \frac{3}{2} k_{\text{iso}} \langle \sin(\theta)^2 \rangle = \frac{3}{2} k_{\text{iso}} P(\theta) \\ k_z &= 3k_{\text{iso}} \langle \cos(\theta)^2 \rangle = 3k_{\text{iso}} [1 - \langle \sin(\theta)^2 \rangle] = 3k_{\text{iso}} [1 - P(\theta)] \end{aligned} \quad (\text{SI-2.2})$$

Where $P(\theta)$ is the order parameter. In the region of spectral absorption, the dispersion of the real part of the refractive index can be determined via the Kramers-Kronig relation^[3]

$$n_1(w) = n_\infty + \frac{2}{\pi} \int_0^\infty \frac{x \cdot k(x)}{x^2 - w^2} dx \quad (\text{SI-2.3})$$

Using this model the reflection of the film at a given incidence angle, α_0 , and wavelength, λ , depends of four experimental parameters; film thickness (d), reflective index, n_1 , k_{iso} and $P(\theta)$. From theory, a wide range of experimental measurements of ΔR_p and ΔR_s as a function of α_0 would allow the determination of the four parameters of the described model, i. e., k_{iso} , $P(\theta)$, d and n_1 by numerical fitting. However, this information cannot be accessed due to experimental limitations. These limitations can be overcome

by separately measuring or estimation of n_∞ and d . Thus, a value, $n_\infty = 1.6$ has been assumed, and the film thickness was estimated from CPK models, taking into account the molecular area given by the compression state of each Langmuir monolayer, obtaining $d \approx 2$ nm.

Under normal incidence the reflection spectrum depend on three parameters, k_x , n_1 and d , exclusively, but not depending on k_{iso} and $P(\theta)$ in a separate way.^[2] This behavior can be used to determine the dependence of n_1 with λ . This procedure has been applied as follows; first, an approximate k_x value from the reflection spectrum under normal incidence and high surface pressure (ΔR_n , unpolarized radiation) has been determined from the following expression:

$$k_x^0 \approx \frac{3}{2} \frac{\lambda \cdot \Delta R_n}{8\pi \cdot d \cdot \sqrt{R_s}} \quad (\text{SI-2.4})$$

Where, $R_s \approx 0.02$ is the reflection of in the absence of the Langmuir monolayer. From this set of k_x^0 values, a first set of n_1^0 values was obtained solving numerically the integral (SI-2.3).^[3] With these sets of k_x^0 and n_1^0 values the reflection spectrum under normal incidence ΔR^0 , is simulated and compared with the experimental one, ΔR_n . Next, a new set of k_x values could be obtained from the relationship $k_x^1 = k_{iso}^0 \times (\Delta R_n / \Delta R^0)$, and next n_1^1 could be obtained applied again equation (SI-2.3). These corrected k_x^1 and n_1^1 values are used for a new correction, and the process being repeated until experimental and theoretical reflections match. Four iterations are enough to obtain calculated results showing a quite good agreement with the experimental values of reflection under normal incidence. k_x and n_1 values obtained for $\pi = 38$ mN/m are shown in Figure SI.2.1.

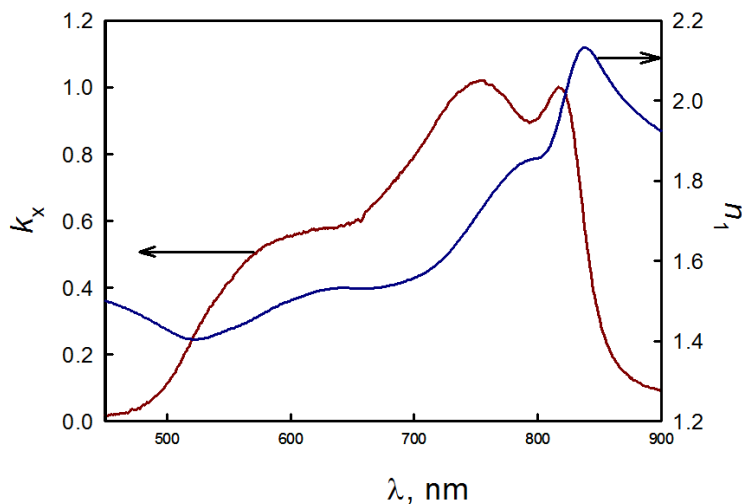


Figure SI.2.1: k_x and n_1 values obtained from the reflection spectrum under normal incidence. $\pi = 38$ mN/m.

In the next step, the wavelengths corresponding to each absorption maxima are selected, and the values of n_1 according to the results shown in the figure SI.2.1 are fixed. Thus, for $\lambda = 600$ nm, 760 nm and 822 nm, the n_1 values were 1.5, 1.75 and 2.01, respectively. Then, once fixed d and n_1 , the k_{iso} and $P(\theta)$ values are obtained by fitting the experimental data to the theoretical model, following the procedure described previously.^[2] The ΔR values for different angles of incidence and s-and p radiation are used as input experimental data.

The experimental ΔR_s and ΔR_p values at the absorption maxima, $\lambda = 600$ nm, $\lambda = 760$ nm and $\lambda = 822$ nm at $\pi = 38$ mN/m, are shown in Figures S2.2, S2.3 and S2.4, respectively (circles). The solid lines in Figure SI.2.2, SI.2.3 and SI.2.4 correspond to the theoretical predictions for the values of the obtained parameters after the numerical fitting. Thus, $k_{\text{iso}} = 0.38 \pm 0.04$ and $P(\theta) = 0.95 \pm 0.09$, for $\lambda = 600$ nm, $k_{\text{iso}} = 0.58 \pm 0.07$ and $P(\theta) = 1.0 \pm 0.1$, for $\lambda = 760$ nm and $k_{\text{iso}} = 0.62 \pm 0.07$ and $P(\theta) = 0.9 \pm 0.1$, for $\lambda = 822$ nm are obtained.

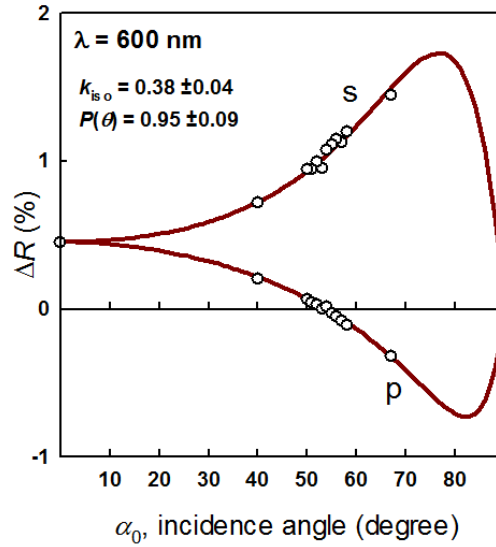


Figure SI.2.2: Circles: Experimental ΔR_s and ΔR_p of the OTCC monolayer, correspond at $\lambda = 600$ nm for $\pi = 28$ mN/m The solid lines correspond to the theoretical variation of ΔR_s (s) and ΔR_p (p) vs α_0 for $n_1 = 1.5$, $d = 2$ nm, $k_{iso} = 0.38$ and $P(\theta) = 0.95$.

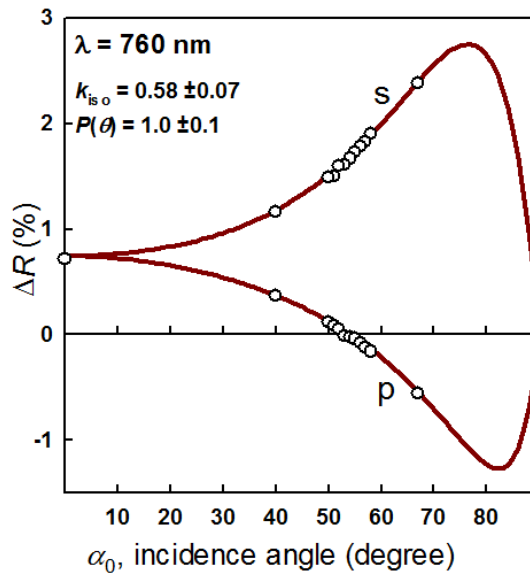


Figure SI.2.3: Circles: Experimental ΔR_s and ΔR_p of the OTCC monolayer, correspond at $\lambda = 760$ nm for $\pi = 28$ mN/m The solid lines correspond to the theoretical variation of ΔR_s (s) and ΔR_p (p) vs α_0 for $n_1 = 1.75$, $d = 2$ nm, $k_{iso} = 0.58$ and $P(\theta) = 1.0$.

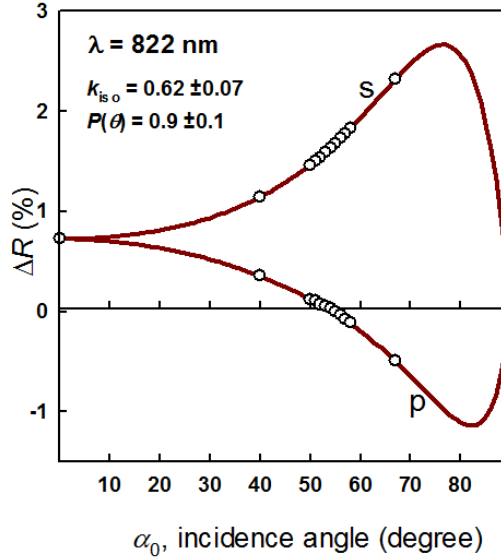


Figure SI.2.4: Circles: Experimental ΔR_s and ΔR_p of the OTCC monolayer, correspond at $\lambda = 822$ nm for $\pi = 28$ mN/m. The solid lines correspond to the theoretical variation of ΔR_s (s) and ΔR_p (p) vs α_0 for $n_1 = 2.01$, $d = 2$ nm, $k_{iso} = 0.62$ and $P(\theta) = 0.9$.

2.5.1.2 The physical origin of the in-plane anisotropy: relationship between reflectivity and ϕ angle

As obtained in the previous section, $P(\theta) \approx 1$, and therefore $\theta \approx 90^\circ$. In these circumstances equations (SI-2.1) can be expressed as:

$$k_x = 3k_{iso} \langle \cos(\phi)^2 \rangle$$

$$k_y = 3k_{iso} \langle \sin(\phi)^2 \rangle$$

$$k_z = 0$$

Figure SI.2.5 (continuous line) shows the reflection under p-polarized radiation, according to Fresnel's equations, for a typical film in which $\theta \approx 90^\circ$, $n_1 = 1.6$, $d = 2$ nm, $k_{iso} = 0.5$ and $\lambda = 600$ nm, being $\alpha_0 = 53.15^\circ$ (Brewster angle).

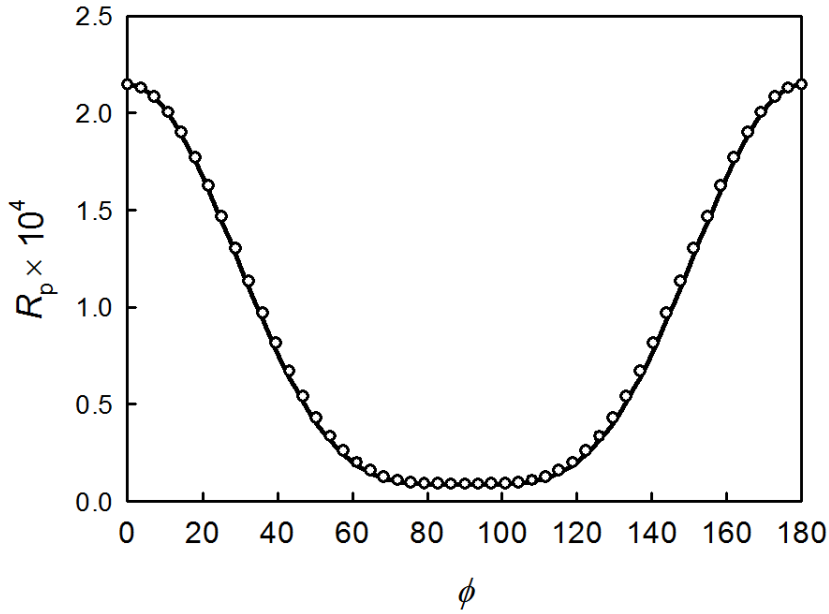


Figure SI.2.5: Plot of R_p , vs ϕ angle (Continuous black line), according to Fresnel's equations, for $\theta = 90^\circ$, $n_1 = 1.6$, $d = 2$ nm, $k_{iso} = 0.5$, $\lambda = 600$ nm, and $\alpha_0 = 53.15^\circ$ (Brewster angle). Circles: Plot of equation (SI-2.5) vs ϕ angle.

In Figure SI.2.5, is also represented (circles) the equation:

$$R_p = A \times \cos(\phi)^4 + B = [R_p(\phi = 0^\circ) - R_p(\phi = 90^\circ)] \times \cos(\phi)^4 + R_p(\phi = 90^\circ) \tag{SI-2.5}$$

Where A and B, are constants related to the reflections at 0 and 90 degrees, as shown in the Equation (SI-2.5). A quite good agreement between the calculated values from Fresnel equations and equation (SI-2.5) is obtained. Using equation (SI 2.5) to replace the Fresnel equations at the Brewster angle is correct provided that $\theta = 90^\circ$ and $k_{iso} \leq 2$.

Equation (SI-2.5) allows us to establish a simple relationship between the transition dipole orientation (ϕ angle) and the intensity of each pixel of BAM image (0-255 gray scale) as described in manuscript.

2.5.2. Dichroic ratio of the Langmuir-Schaefer films

The OTCC monolayers could be transferred onto solid substrates by horizontal lifting or Langmuir-Schaefer method. The monolayers were transferred at $\pi = 12$ mN/m, with the transfer ratio being close to unity in all the cases. To estimate the average tilt of the transition dipoles with respect to the surface, absorption spectra under s-(blue line) and p-(red line) polarized light at 45° of incidence angles were recorded (Figure SI.2.6).

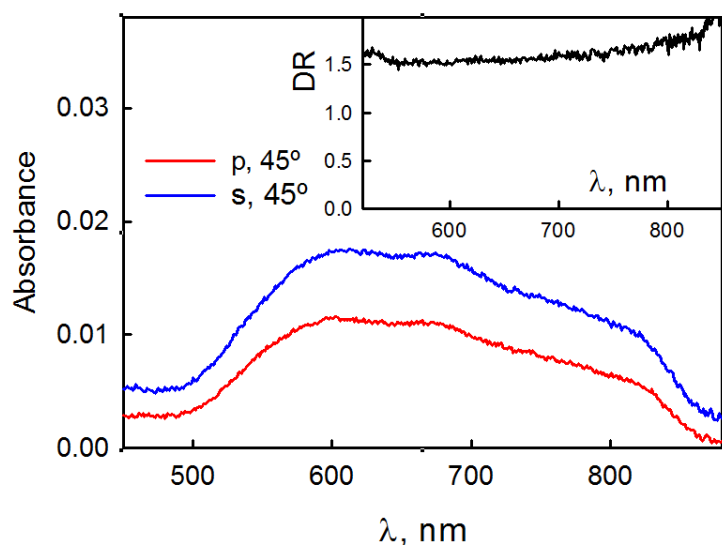


Figure SI.2.6. Polarized absorption spectra, s (blue line) and p (red line), under 45° incidence angle of the OTCC LS film (one monolayer). Inset: Variation of DR.

The spectra obtained are slightly different from those obtained at the same surface pressure at the air-water interface (see DR yellow line in Figure SI.2.4, manuscript), presumably due to a partial disaggregation, though all absorption bands are clearly recognizable. The results can be interpreted by using the dichroic ratio, $DR = A_{b_s}/A_{b_p}$ (see Inset in Figure SI.2.6). Thus, for an incidence angle of 45° , $DR \approx 1.6 \pm 0.1$ in the range 550-820 nm. The measurement was repeated four times, showing good reproducibility.

For very thin films containing molecules with non-degenerated transition dipole components, and according Vandevyver et al. we can write:^[4]

$$DR = \frac{Ab_s}{Ab_p} \approx \frac{n_0 \cos(\alpha_2) + n_2 \cos(\alpha_0)}{n_0 \cos(\alpha_0) + n_2 \cos(\alpha_2)} \left[\frac{n_0^3 n_2 \sin(\alpha_0)^2}{n_1^4} \left(\frac{2 \langle \cos(\theta)^2 \rangle}{\langle \sin(\theta)^2 \rangle} \right) + \cos(\alpha_0) \cos(\alpha_2) \right]^{-1}$$

(SI- 2.6)

Where, θ represents the angle between the single transition dipole and the normal to the plane support (and the rest of parameters are defined in Scheme SI.2.1). This equation is obtained under the consideration that the films are isotropic in the support plane, which has been experimentally verified by recording different absorption spectra of the LS films under normal incidence and rotating the linear polarized light, and similar spectra in all the experiments were obtained.

On quartz the previous equation predicts $DR = 1.57$ for $\theta = 90^\circ$ independently of the n_1 value, in very good agreement with the obtain result. This result confirm that all the absorption component are polarized in the interface plane, even the disaggregate OTCC.

2.5.3. References

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Conclusiones



Al final de cada uno de los capítulos de esta Memoria, se incluyen un conjunto de conclusiones particulares al estudio desarrollado. En este apartado se presentan las conclusiones generales, teniendo en cuenta el grado de avance alcanzado:

1. Se han fabricado con éxito monocapas mixtas con un alto grado de ordenación a nivel molecular mediante una estrategia novedosa que consiste en emplear mezclas equimoleculares formadas por una matriz de fosfolípido y un colorante orgánico. De esta manera, se ha demostrado que dichos componentes deben reunir una serie de características que ayuden a la formación de estructuras bien organizadas como son; tener cadenas alquílicas de similar longitud para lograr un buen empaquetamiento, poseer cabezas polares de carga opuesta para que las interacciones electrostáticas compensen la repulsión entre los momentos dipolares de las moléculas, un adecuado balance entre las áreas que ocupan las cadenas hidrófobas y los grupos polares, así como que los grupos polares permitan la agregación lateral de la monocapa.

2. Se ha observado que el fenómeno de colapso para determinadas películas, no está ligado al desorden ni a la desestabilización de la monocapa. Por el contrario, se ha encontrado en monocapas mixtas DAO:SA 1:1 que este fenómeno supone un cambio de fase a estructuras con una mayor organización molecular, formándose una estructura 3D en la interfase aire-agua.

3. Se ha logrado un cierto grado de control sobre la forma y tamaño de los dominios formados en la interfase aire-agua (ordenación, agregación, orientación y conformación molecular) mediante la aplicación de factores externos como presión y velocidad de compresión sobre la película. Así por ejemplo ha sido posible controlar la gran diversidad de formas y tamaños de las estructuras supramoleculares quirales observadas en la monocapa mixta del derivado de quinoleína (MQ) y un fosfolípido amónico (DMPA).

4. Se ha demostrado que la caracterización *in situ* de estructuras bidimensionales bien definidas formadas tanto en la interfase aire-agua como transferidas sobre soportes sólidos, a través de técnicas ópticas como BAM y espectroscópicas como PM-IRRAS, GIXD, UV-Vis RS y RAV, así como fluorescencia y/o dicroísmo circular, respectivamente, complementada con el uso de simulaciones computacionales y modelos teóricos, ofrece una extraordinaria posibilidad para la elucidación de la organización molecular de esas películas en las diferentes interfases.

Resumen



Uno de los objetivos de la química supramolecular ha sido y sigue siendo el desarrollo de métodos o estrategias para construir películas orgánicas ordenadas en estructuras bien definidas y de gran extensión. A escala nanoscópica, las propiedades físicas de estos sistemas moleculares se determinan mediante las relaciones entre su composición química, estructura y la organización de los materiales utilizados. En particular, cuando las moléculas que forman esos sistemas tienden a la agregación, también se ven afectadas sus características moleculares. De hecho, las consecuencias más importantes de la agregación molecular de colorantes orgánicos no son sólo los cambios químicos que se producen, sino principalmente los cambios detectados en las propiedades ópticas de las unidades cromóforas que interactúan entre sí.

Ante este hecho es necesario buscar nuevas estrategias para la construcción de estructuras bi-dimensionales bien definidas en superficies (interfases) donde se facilite el control de la organización de los componentes de esos bloques moleculares. En este marco, la interfase aire-agua se constituye como interfase modelo donde la organización lateral es controlada mediante la preparación de películas delgadas. En estas películas ultrafinas mixtas, se seleccionan los componentes sobre la base de la formación de interacciones atractivas entre ellos, estableciendo la conexión lateral entre los mismos a través de la auto-agregación de los colorantes. Una estrategia para lograr esta conexión lateral es establecer un balance adecuado entre el tamaño de los grupos hidrofóbicos y los grupos polares.

En este contexto mediante ciertos métodos experimentales se pueden formar películas con propiedades estructurales y ópticas bien definidas compuestas por mezclas de colorantes y lípidos. De esta forma, se preparan películas delgadas mixtas mediante el método de Langmuir en la interfase aire-agua y los métodos Langmuir-Blodgett (LB) y Langmuir-Schaeffer (LS) sobre soportes sólidos. Dichas películas mixtas están

formadas por lípidos, tales como ácido 1,2-dimiristoil-*sn*-glicero-3-fosfato DMPA, ácido esteárico SA, y colorantes de carga opuesta como acridinas, cianinas y derivados de las cianinas, cuya estructura molecular les confiere un comportamiento anfifílico (cadenas alquílicas hidrófobas, grupo polar hidrofílico).

Para poder estudiar y caracterizar estas películas delgadas mixtas es necesario disponer de técnicas que nos aporten información tanto de la organización de la parte polar, como de las cadenas alquílicas. No obstante, la mayoría de las técnicas de caracterización de monocapas Langmuir están centradas en el estudio y organización de las cadenas alquílicas que conforman el sistema, como la Espectroscopía infrarroja de absorción-reflexión con modulación de polarización (PM-IRRAS) , la técnica de Difracción de rayos X de incidencia rasante (GIXS) y la técnica de Reflectividad especular de rayos X (XRR), siendo más escasas aquellas que proporcionan información directa de la organización del grupo polar. Por todo ello es necesario desarrollar técnicas ópticas como la Microscopía de ángulo Brewster (BAM) y espectroscópicas como la Espectroscopía de Reflexión UV-visible bajo ángulo variable y luz polarizada (RAV) con el objetivo de obtener información útil acerca de la organización de las unidades moleculares que conforman la región polar y el uso de otras técnicas complementarias (fluorescencia, dicroísmo circular), que aumenten el abanico de potenciales aplicaciones de estas películas.

Por otra parte, es importante resaltar la utilización de técnicas de simulación en ordenador, así como el desarrollo de modelos teóricos y matemáticos en el sentido de validar y complementar los datos obtenidos experimentalmente.

En esta Tesis se estudia la formación de agregados moleculares de colorantes orgánicos en películas delgadas, que es un importante factor a considerar dado que estos agregados moleculares son estructuras

autoensambladas de moléculas sencillas que presentan propiedades ópticas significativamente alteradas con respecto a las moléculas individuales. Por ello, i.e. por su importante papel en el diseño de dispositivos moleculares, la preparación de películas orgánicas ultrafinas con estructuras bien definidas ha atraído el interés de la comunidad científica. En este marco, el control de la organización molecular es uno de los objetivos esenciales de la llamada Química Supramolecular.

La primera parte de esta Tesis va dirigida al estudio del fenómeno de colapso de la película formada por el colorante orgánico N-10-dodecil naranja de acridina (DAO) y ácido esteárico (SA) en relación equimolecular. La aproximación "botton-up" (i.e. autoagregación de bloques de construcción individuales en estructuras funcionales más grandes) es fundamental en nanotecnología. En este marco, las transformaciones controladas de entidades 2D a estructuras más complejas 3D en la nanoescala se ha destacado como una adecuada alternativa para la construcción de material multifuncional.

Precisamente, el colapso de monocapas de Langmuir resulta de gran relevancia desde el punto de vista nanotecnológico, dado que durante este proceso las moléculas son ensambladas en estructuras 3D supramoleculares. Asimismo, el colapso de una monocapa juega un papel fundamental en procesos biológicos relevantes (e.g. surfactantes pulmonares en el ciclo de la respiración). La fuerte tendencia de la acridina para agregarse y formar estructuras en la interfase aire-agua, junto a sus propiedades cromóforas, hace que sea un sistema ideal para este tipo de estudio mediante técnicas ópticas como BAM, y espectroscópicas como Reflexión UV-visible, además de estudiar el empaquetamiento de las cadenas durante la tricapa formada en el colapso mediante PM-IRRAS y XRR.

Adicionalmente a esta investigación, en esta Tesis se ha estudiado el fenómenos de agregación de la tiocarbocianina anfifílica (OTCC) y el

derivado de esta, la quinoleína anfifílica (MQ).

Como se ha descrito anteriormente, la interfase aire-agua es un excepcional sistema donde el confinamiento 2D de moléculas anfifílicas impone restricciones geométricas a los agregados moleculares que se forman. El confinamiento bidimensional puede inducir la quiralidad de moléculas proquirales. La quiralidad supramolecular es el resultado de un adecuado empaquetamiento molecular debido a la agregación, i.e., la aproximación "botton-up". De esta manera, algunas moléculas aquirales podrían formar ensamblajes quirales en la interfase aire-agua.

Las estructuras quirales 2D supramoleculares en la interfase aire-agua pueden ser evaluadas in situ mediante BAM. El control del tamaño, forma y periodicidad de los dominios en la interfase es de gran interés debido a que las superficies mesoscópicas estructuradas pueden servir como plataformas en la ingeniería de interfases biológicas y en la construcción de estructuras biofuncionalizadas y sistemas programados.

Un grado de mayor avance en la fabricación de estas películas es poder controlar la agregación, así como orientación e incluso la morfología y tamaño de las estructuras formadas. Durante el proceso de compresión puede realizarse fácilmente la evaluación de la formación de agregados y la orientación molecular en las monocapas por espectroscopía de reflexión UV-vis, y microscopía de ángulo Brewster (BAM)

Las estructuras supramoleculares observadas en la monocapa mixta de derivado de quinoleína (MQ) y un fosfolípido aniónico (DMPA) muestran estructuras quirales inusuales con gran diversidad de formas y tamaños. Mediante un procedimiento experimental, en el cual se aplica una secuencia de presiones superficiales en distintos pasos y diferentes velocidades de barrido se ha mostrado una posible vía para controlar el tamaño y forma de los dominios, obteniendo dominios homogéneos. Asimismo, este control en la morfología de las películas ha sido posible elucidando previamente el proceso de nucleación y crecimiento de esas

estructuras mediante las transiciones de fase de las isothermas. Como complemento a los resultados experimentales, también se han usado modelos teóricos como la aproximación de los dipolos extendidos y simulaciones computacionales empleando mecanismos moleculares que confirman la fuerte tendencia del grupo quinoleína para formar agregados quirales.

Finalmente se ha estudiado el fenómeno de agregación en el sistema formado por la cianina anfifílica (OTCC). En la elucidación de cómo los detalles estructurales determinan las propiedades ópticas, los investigadores plantean el cambio de las propiedades de los materiales alterando el empaquetamiento molecular en la nanoestructura del ensamblaje. Las propiedades estructurales de los agregados de colorante pueden ser relacionadas con el empaquetamiento molecular de los cromóforos. Los colorantes de la familia de las cianinas bajo ciertas condiciones estructurales presentan agregados H y J (agregados con desplazamiento de la banda de absorción a menores y mayores longitudes de onda respectivamente con respecto al monómero) que han tenido gran aplicabilidad como material fotográfico, moléculas antena, sistemas de transferencia de energía aceptor-receptor, etc. Ante esta perspectiva es de gran importancia estudiar los diferentes agregados que forman las cianinas, los cuales no siempre responden a los modelos simples de agregación H y J, apareciendo bandas complejas con distinta polarización.

Sobre esta base y las perspectivas de aplicación de las cianinas se han preparado y caracterizado monocapas de OTCC, mediante el uso de la técnica ΔR , ΔR -AV y BAM.

Una técnica ideal para el estudio de colorantes en la interfase aire-agua es la Espectroscopía de Reflexión UV-Vis, cuyo uso ha estado limitado tradicionalmente a incidencia normal, debido a la simplicidad del tratamiento teórico requerido. Mediante esta técnica de Reflexión es posible resolver bandas con diferente polarización, ya que la banda de

absorción se descompone en una parte positiva y otra negativa en función de la polarización de sus componentes. Ante estas circunstancias, en esta tesis se ha propuesto un nuevo método de análisis basado en las expresiones de reflectividad (R) obtenidas a partir de las ecuaciones de Fresnel. Gracias a este método, es posible conocer el valor del parámetro de orden (relacionado con el ángulo de inclinación del cromóforo), o analizar aquellos sistemas que no pueden ser resueltos mediante el método tradicional de incidencia normal.

Para estudiar la existencia de dipolos con diferente orientación en el sistema se realizaron experiencias en BAM, usando láseres de diferente longitud de onda. A su vez se propone un procedimiento matemático que permite simular las diferentes texturas de los dominios observados en las imágenes BAM, dando información estructural acerca de sus componentes, tal como inclinación y disposición de las moléculas. Las estructuras supramoleculares observadas mediante la técnica de BAM en la monocapa de derivado de cianina (OTCC) muestran la formación de un único tipo de dominio con anisotropía interna.

La influencia de la agregación de las moléculas de OTCC en sus propiedades ópticas ha sido investigada mediante fluorescencia y CD en películas LB y LS. Así se realizaron transferencias que permiten depositar las moléculas orgánicas sobre diferentes soportes sólidos, formando sistemas organizados con el espesor deseado y con una orientación molecular bien definida, y preparar estructuras supramoleculares heterogéneas mediante la deposición sucesiva de monocapas de distinta naturaleza.

En esta Tesis se han fabricado con éxito monocapas mixtas con un alto grado de ordenación a nivel molecular mediante una estrategia novedosa que consiste en emplear mezclas equimoleculares formadas por una matriz de fosfolípido y un colorante orgánico. De esta manera, se ha

demostrado que dichos componentes deben reunir una serie de características que ayuden a la formación de estructuras bien organizadas como son; tener cadenas alquílicas de similar longitud para lograr un buen empaquetamiento, poseer cabezas polares de carga opuesta para que las interacciones electrostáticas compensen la repulsión entre los momentos dipolares de las moléculas, una parecida relación entre las áreas que ocupan las cadenas hidrófobas y los grupos polares, así como que los grupos polares permitan la agregación lateral de la monocapa.

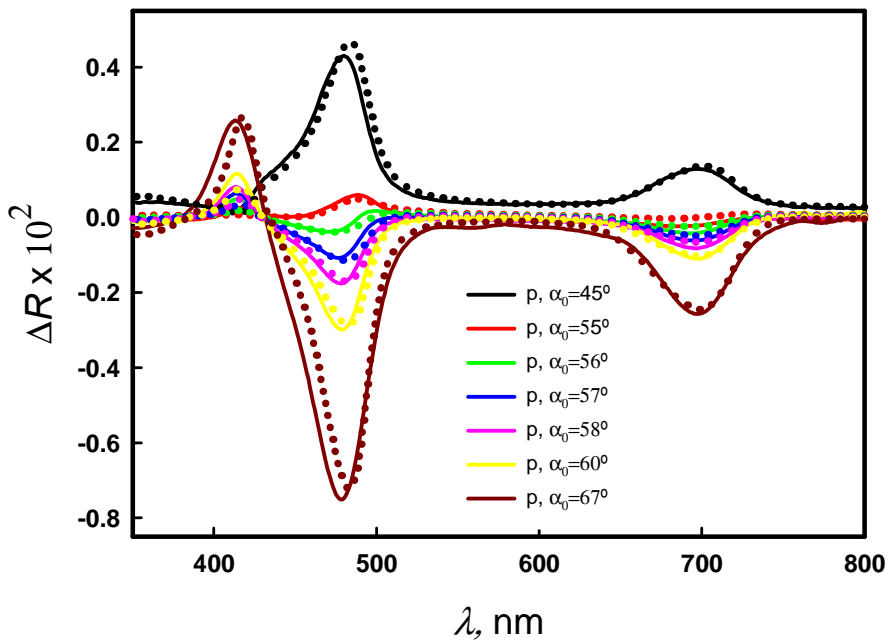
A su vez también se ha logrado un cierto grado de control sobre la forma y tamaño de los dominios formados en la interfase aire-agua (ordenación, agregación, orientación y conformación molecular) mediante la aplicación de factores externos como presión y velocidad de compresión sobre la película. Así por ejemplo ha sido posible controlar la gran diversidad de formas y tamaños de las estructuras supramoleculares quirales observadas en la monocapa mixta del derivado de quinoleína (MQ) y un fosfolípido amónico (DMPA).

Adicionalmente en esta Tesis se ha estudiado el fenómeno de colapso, y se ha observado que para determinadas películas, no está ligado al desorden ni a la desestabilización de la monocapa. Por el contrario, se ha encontrado en monocapas mixtas DAO:SA 1:1 que este fenómeno supone un cambio de fase a estructuras con una mayor organización molecular, formándose una estructura 3D en la interfase aire-agua en la que aparecen dominios hexagonales con anisotropía interna.

Finalmente, se ha demostrado que la caracterización *in situ* de estructuras bidimensionales bien definidas formadas tanto en la interfase aire-agua como transferidas sobre soportes sólidos, a través de técnicas ópticas como BAM y espectroscópicas como PM-IRRAS, XRR, UV-Vis RS y RAV, así como fluorescencia y/o dicroísmo circular, respectivamente, complementada con el uso de simulaciones computacionales y modelos teóricos, ofrece una extraordinaria posibilidad

para la elucidación de la organización molecular de esas películas en las diferentes interfases.

Otras aportaciones durante la tesis



UV-Vis Reflection-Absorption Spectroscopy at air-liquid interfaces

ABSTRACT

UV-Visible Reflection-Absorption Spectroscopy (UVRAS) technique is introduced with a general perspective on fundamental and applications. UVRAS is formally identical to IR reflection-absorption spectroscopy (IRRAS), and therefore the methodology developed for this IR technique can be applied in the UV-visible region. UVRAS can be applied to air-solid, air-liquid and liquid-liquid interfaces. This review focuses on the use of UVRAS for studying Langmuir monolayers. We introduce the theoretical framework for a successful understanding of the UVRAS data, and we illustrate the usage of this data treatment to a previous study from our group comprising an amphiphilic porphyrin. For ultrathin films with a thickness of few nm, UVRAS produces positive or negative bands when p-polarized radiation is used, depending on the incidence angle and the orientation of dipole absorption. UVRAS technique provides highly valuable information on tilt of chromophores at the air-liquid interface, and moreover allows the determination of optical parameters. We propose UVRAS as a powerful technique to investigate the in situ optical properties of Langmuir monolayers.

1. INTRODUCTION

UV-Visible Reflection Spectroscopy (UV-Vis-RS) at the air-liquid interface was developed by D. Möbius et al. in the mid-80s [1-3]. This technique can be applied not only to air-liquid interfaces, but also to air-solid interfaces. The experimental measurement records the difference between the reflection of incoming light from a clean air-liquid interface and an air-liquid interface covered by a Langmuir monolayer containing chromophores. This experimental measurement is often named as ΔR . Gibbs [4] and Langmuir monolayers have been studied by UV-Vis-RS [5].

There is abundant literature on the use of UV-Vis-RS at the air-water interface, in the study of ionic interactions [6-10], molecular recognition [11-14], formation of inclusion complexes [15], or the study of phenomena such as photochromism [16-18], photoisomerization [19-25], charge and energy transfer [26-31], and photoinduced electron-transfer [32-35]. Moreover, the UV-Vis-RS has been used in studying the interactions of various soluble components in the aqueous subphase, as drugs [36, 37], proteins [38-40] and polyelectrolytes [41-43], with ordered lipid Langmuir monolayers. Remarkably, UV-vis RS is nowadays intensively used for studying a wide range of Langmuir monolayers. We highlight sound studies concerning liquid-crystal forming molecules [44-46], molecular wires [47], and porphyrin derivatives [48-50], having a large interest in sensing,[51-53] see Figure 1.

The ΔR measurement provides information on the chromophores tilt and aggregation at the air-liquid interface [44, 45, 54-72]. However, in spite

of the enormous potential of this technique, the applications of the UV-Vis-RS have been limited mainly to reflection measurements under light normal incidence (LNI). Only a few studies under light variable incidence (LVI) have been realized, being restricted to incidence angles lower than the Brewster angle [2, 3, 73].

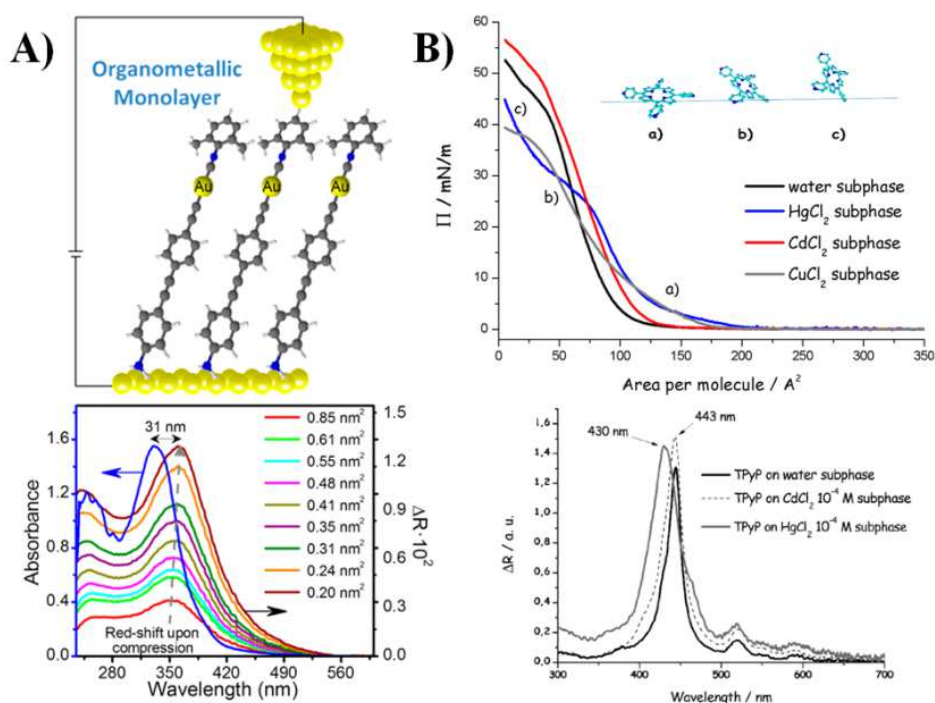


Figure 1 A) A Langmuir monolayer of an organometallic oligo(phenylene)ethynylene derivative was studied by UV-vis reflection spectroscopy. Based on the knowledge of the intermolecular interactions at the air-water interface, the behavior of this layer once transferred to a solid support show features of molecular wires [47]. Copyright from American Chemical Society, 2015. B) Langmuir monolayers of a tetrapyrrolyl-substituted porphyrin have shown a large selectivity in sensing Cu²⁺ toward Hg²⁺ ions present in the subphase. UV-vis reflection spectroscopy provided unique experimental evidence on the detailed interaction of the metallic ions with the porphyrin; whereas Hg²⁺ ions interact with both the pyridyl substituents and the central bite of the ring inducing H-aggregation, Cu²⁺ ions interact with only the porphyrin peripheral substituents. This highly detailed information on intermolecular interactions is most valuable when designing sensing devices [52]. Copyright from American Chemical Society, 2014.

Recently, UV-Vis-RS under LVI angle with s- and p- polarized radiation has been developed [74]. UV-Vis-RS is formally identical to IR reflection-absorption spectroscopy (IRRAS) on semi-transparent substrates [75-78]. Thus, the methodology developed for this IR technique can be readily applied in UV-visible region. For ultrathin films of thickness of a few nm, UV-Vis-RS renders positive or negative bands when p-polarized radiation is used, as a function of the incidence angle and the orientation of dipole absorption [74], similarly to IRRAS [75]. UV-Vis-RS has proven to be highly sensitive for resolving bands with different polarization [74]. Given the analogy between IRRAS and the UV-Visible Reflection Spectroscopy, we rename this last technique as UVRAS (UV-Visible Reflection-absorption Spectroscopy), denomination that we use hereinafter.

In this review, the UVRAS technique is outlined in a general way, extending the previous treatment [74], to thin films formed by biaxial anisotropic stratified layers. To illustrate the huge potential of UVRAS, we review with great detail in the data treatment a previous study published by our group [79, 80]. In that study, the splitting of the Soret band of an amphiphilic porphyrin at the air-water interface is studied as a function of surface pressure. The Soret band of a given porphyrin can be described in terms of two perpendicular oscillators, B_x , and B_y . The symmetry of a freebase porphyrin is D_{4h} , and the Soret band is degenerate [81]. However, sometimes degeneration is lost for densely packed porphyrins as a function of

the molecular organization and the Soret band undergoes a splitting process [82-84].

2. THEORY

2.1 Reflection at the air-liquid interface under light normal incidence (LNI)

When studying monolayers deposited on solid supports, the radiation incidence angle have to be changed to determine the chromophores tilt. However, using Langmuir monolayers in principle one can modulate the chromophores tilting by applying surface pressure. Therefore, at least in some cases, LNI can provide information about the chromophores tilt.

Under LNI, the absorption by a film located on the top of a given interface increases the total reflection of radiation at this interface. In case the absorption is small, i. e., less than 0.05 percent of the incident radiation, as usually found in Langmuir monolayers [1]:

$$\Delta R_n = R_{D,S} - R_S \approx \sqrt{R_S} \cdot A_s \quad (1)$$

Where ΔR_n is the increase of reflection under normal incidence, R_S and $R_{D,S}$ are the intensities of reflection of incoming radiation in the absence and presence of a Langmuir monolayer, respectively, and A_s is defined as the absorption of incident radiation from the Langmuir monolayer. The above relationship can be also expressed by [54, 58]:

$$\Delta R_n \approx 2.303 \times 10^3 f_o \varepsilon \sqrt{R_S} \Gamma \quad (2)$$

Where ε is the molar absorption coefficient with units $M^{-1} \cdot cm^{-1}$, Γ is the surface concentration in $mol \cdot cm^{-2}$, and f_o is the orientation factor. The orientation factor compares the average orientation of the dipole transition at the air-liquid interface with respect to the orientation in bulk solution, and its mathematical expression will be defined below.

The influence of surface concentration in the reflection spectrum can be eliminated by normalizing that given spectrum by the surface area [58]:

$$\Delta R_n^N = A \times \Delta R_n = \frac{2.303 \times 10^{17} f_0 \varepsilon}{N_A} \sqrt{R_S} = 5.41 \times 10^{-8} f_0 \varepsilon \quad (3)$$

Where A is the area occupied per chromophore molecule, N_A is Avogadro's number. $R_S = 0.02$ has been used as the reflection value for the bare air-liquid interface. ΔR_n^N is expressed in $\text{nm}^2 \cdot \text{molecule}^{-1}$.

Equation (3) provides a method to detect the presence of chromophores at the air-liquid interface using UV-vis reflection spectroscopy measurements. ΔR is the increase of reflection of incoming radiation in a Langmuir monolayer-covered air-liquid interface with respect to the bare air-liquid interface. The amount of chromophore can be effectively quantified by this measurement. Moreover, information about the orientation of the chromophore can be obtained. Typically, ΔR_n values are about 10^{-3} , so they are usually expressed in % ($\Delta R_n \times 100$). For example, if $\varepsilon = 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$, and $A = 1 \text{ nm}^2$ ($\Gamma = 1.67 \times 10^{-10} \text{ mol/cm}^2$), a value of $\Delta R_n(\%) = 0.54$ is obtained.

The equation (2) ultimately aims at the comparison of the UV-vis reflection at the air-liquid or air-solid interfaces and the bulk spectra in solution. Unfortunately, this comparison cannot be performed in a simple way given the molecular aggregation of the chromophores at the air-liquid interface. The aggregation of the chromophores results in significant variations of $\varepsilon(\lambda)$. The effect of these variations in $\varepsilon(\lambda)$ can be assessed by relating the values of the oscillator strength in both media, i. e., air-liquid interface and bulk solution.

The intensity of an electronic absorption band is usually represented in terms of the so-called oscillator strength, f [85],

$$f = \frac{4\varepsilon_0 2.303 m_e c_0}{N_A e^2} \int_{\text{band}} \varepsilon \cdot d\nu = 1.44 \times 10^{-19} \int_{\text{band}} \varepsilon \cdot d\nu \quad (4)$$

Where ε_0 is the vacuum permittivity, m_e and e are the electron mass and charge, respectively, and c_0 is the speed of light in vacuum. The numerical factor 1.44×10^{-19} has units of $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm} \cdot \text{s}$. A method for calculating the apparent oscillator strength (f_{ap}) through the integration of normalized reflection band can be obtained by combining equations (3) and (4),

$$f_{\text{ap}} = f \times f_0 = 2.66 \times 10^{-12} \int_{\text{band}} \Delta R_n^N d\nu \quad (5)$$

Where the factor 2.66×10^{-12} has units of $\text{nm}^{-2} \cdot \text{s}$. Note that in the above definition, f is the oscillator strength in solution, i. e., isotropic conditions. According to the Davidov model corresponding to excited states of weakly interacting molecules, oscillator strength is preserved in different aggregation state [86, 87]. In such a case, the variations of f_{ap} provide a direct measurement of the orientation factor, f_0 , at the air-liquid interface. The equation (5) has been applied to a number of different Langmuir monolayers, allowing a correct estimate of the average orientation of the transition dipoles at the air-water interface [45, 58-60, 62-66, 71]. This method is referred as LNI.

The LNI method cannot be applied in certain cases, as: bands overlapping with different transition dipoles orientations, or oscillator strength

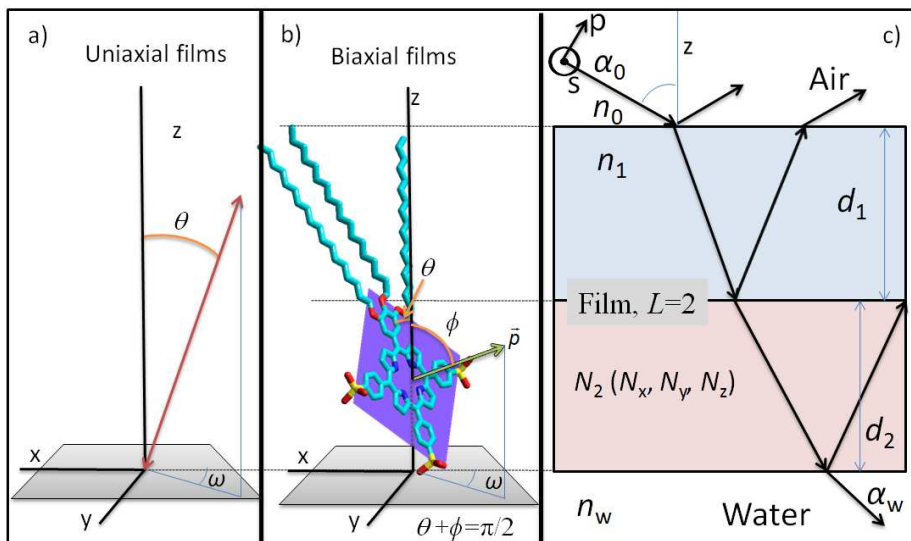
not preserved with compression of the Langmuir monolayer. These limitations have been usually overcome by transferring the Langmuir monolayers to a solid support, and subsequently analyzing the transmission spectra with incident s- and p- polarized radiation under different incidence angles [72, 88]. However, the transference of the Langmuir monolayer to a solid support can result in significant variations of the molecular arrangement within the monolayer. A method allowing the determination of the order parameter in situ at the air-liquid interface is therefore most desirable.

2.2 Reflection at the air-liquid interface under inclined radiation incidence.

We used the Yamamoto and Ishida[89] expressions for the reflection of s- and p- polarized radiation under different incidence angle (α_0) originated for a anisotropy biaxial film formed by L stratified layers between two isotropic media, e g., air and water (see Appendix). Herein we assume that the Langmuir monolayer is spatially ordered long the z axis. In this way, the film could be decomposed into L ideal layers of increasing hydrophilic character (in the air to water direction), such as alkyl chains regions and polar group regions. As a general rule, one can assume that the chromophore group responsible for the absorption is exclusively located in one of these layers. Thus, only this layer would display a complex refractive index, represented by: $N_q = n_q + i \times k_q$, where, $q \equiv x, y, z$, being n_q the real part of the reflective index and k_q the absorption constant along each axes. For the rest of the layers, the refractive index has only the real component, n_{jq} .

In the next section we review the UVRAS data of the $(OD)_3TPPS_3$ monolayer at high surface pressure, see section 3.2. At these conditions, the molecules are oriented almost vertically with respect to the air-water interface (see Scheme 1b), allowing us to assume that the Langmuir monolayer can be decomposed into two ideals layers ($L = 2$, See Scheme 1c), the first layer corresponding to the alkyl chains regions, which is assumed isotropic, with a d_1 thickness, nonabsorbent and with a constant refraction index, n_1 , while the second will be assigned to the polar region (chromophore group). This layer is assumed to be anisotropic ($N_q = n_q + i \times k_q$), and with a thickness d_2 . The

relationships between the absorption constant will be established, depending on the monoaxial or biaxial character of the absorbent material.



Scheme 1 Schematic illustration for the coordinate definitions for the transition dipole in the case of a) monoaxial and b) biaxial degenerated films. c) Sketch of the reflection and transmission in an ideal Langmuir film divided in two layers.

2.2.1 Uniaxial films: For non-degenerated absorption mode we can write

$$\begin{aligned}
 k_x &= k_{\max} \langle \sin(\theta)^2 \rangle \langle \cos(\omega)^2 \rangle \\
 [90]: k_y &= k_{\max} \langle \sin(\theta)^2 \rangle \langle \sin(\omega)^2 \rangle \\
 k_z &= k_{\max} \langle \cos(\theta)^2 \rangle
 \end{aligned}
 \tag{6}$$

Where θ is the angle between the normal to the air-liquid interface and the direction of the transition dipole of the absorption band, ω is the azimuthal angle (see Scheme 1a) and the brackets indicate average values. Langmuir monolayers are considered isotropic in the x-y plane. Note that in the case of occurrence of domains within the monolayer, the beam spot size is

significantly larger than those domains, thus averaging the structure of such monolayer. Therefore : $\langle \sin(\omega)^2 \rangle = \langle \cos(\omega)^2 \rangle = 1/2$. Moreover, if we denominated $k_0 = (1/3)k_{\max}$, where k_0 is the absorption constant when the material is distributed isotropically.

$$\begin{aligned} k_x = k_y &= \frac{3}{2}k_0 \langle \sin(\theta)^2 \rangle = \frac{3}{2}k_0 P(\theta) \\ k_z &= 3k_{\text{iso}} \langle \cos(\theta)^2 \rangle = 3k_0 [1 - \langle \sin(\theta)^2 \rangle] = 3k_0 [1 - P(\theta)] \end{aligned} \quad (7)$$

Where $P(\theta) = \langle \sin(\theta)^2 \rangle$ is the order parameter. Under LNI and s-polarized light, the reflection depends exclusively on $k_x = k_y$. In this case, the orientation factor (f_0) introduced in equation (2), is defined by comparison of the average orientation of the dipole transition at the air-liquid interface ($k_x = k_y$) with respect to the orientation in bulk solution (k_0) [58]:

$$f_0 = \frac{k_y}{k_0} = \frac{3}{2} \langle \sin(\theta)^2 \rangle = \frac{3}{2} P(\theta) \quad (8)$$

As previously mentioned, this expression is not useful when there are overlapping bands with different transition dipoles orientations, or more complex phenomena such as the splitting of bands. In these cases the comparison between the reflection and the solution spectra are not possible. In this case $k_x = k_y$ and k_z must be obtained from the s- and p- polarized spectra at different incidence angles. Here, we can determinate $P(\theta)$ by combining equations (7), by means of the following relationship:

$$P(\theta) = \frac{2k_y}{k_z + 2k_y} \quad (9)$$

For a uniaxial distribution of rod-like molecules, like nematic liquid crystal, the orientational order is described by the Saupe matrix element S [91], which could be related with the previous equations by:

$$S = \frac{(3\langle \cos(\theta)^2 \rangle - 1)}{2} = 1 - \frac{3}{2}\langle \sin(\theta)^2 \rangle = 1 - f_0 = \frac{k_z - k_y}{k_z + 2k_y} \quad (10)$$

S is sometimes referred to as the long-axis order parameter [75]. For a random distribution $S = 0$, $f_0 = 1$ and therefore $k_y = k_z$. $S = -0.5$ for a parallel orientation respect to the x-y plane, being in this case $f_0 = 3/2$ and therefore $k_z = 0$. Finally, for a perpendicular orientation respect to the x-y plane $S = 1$, $f_0 = 0$ and $k_y = 0$.

2.2.1 Biaxial degenerated films: For degenerated absorption modes, as the porphyrin Soret band [75, 88]:

$$\begin{aligned} k_x &= \frac{k_{\max}}{2} \left[1 - \langle \cos(\omega)^2 \rangle \langle \sin(\phi)^2 \rangle \right] = \frac{k_{\max}}{2} \left[1 - \frac{\langle \sin(\phi)^2 \rangle}{2} \right] \\ k_y &= \frac{k_{\max}}{2} \left[1 - \langle \sin(\omega)^2 \rangle \langle \sin(\phi)^2 \rangle \right] = \frac{k_{\max}}{2} \left[1 - \frac{\langle \sin(\phi)^2 \rangle}{2} \right] \\ k_z &= \frac{k_{\max}}{2} \left[1 - \langle \cos(\phi)^2 \rangle \right] = \frac{k_{\max}}{2} \left[\langle \sin(\phi)^2 \rangle \right] \end{aligned} \quad (11)$$

Where ϕ is the angle formed between the normal at the interface, and the vector \mathbf{p} , which is defined as perpendicular at the plane formed by the two degenerated absorption modes (see Scheme 1b, porphyrin plane in this case), and ω is the azimuthal angle. The expressions on the right in the previous

equations contained the conditions of x-y plane isotropy, $\langle \sin(\omega)^2 \rangle = \langle \cos(\omega)^2 \rangle = 1/2$.

As the angle between the vector \mathbf{p} , and the plane formed by the two degenerated absorption modes is $\pi/2$, we can defined $\theta = \pi/2 - \square$. In this way, we can write the previous expressions as:

$$\begin{aligned} k_x = k_y &= \frac{3}{2}k_0 \left[1 - \frac{\langle \cos(\theta)^2 \rangle}{2} \right] = \frac{3}{4}k_0 \left[1 + \langle \sin(\theta)^2 \rangle \right] = \frac{3}{4}k_0 [1 + P(\theta)] \\ k_z &= \frac{3}{2}k_0 \langle \cos(\theta)^2 \rangle = \frac{3}{2}k_0 \left[1 - \langle \sin(\theta)^2 \rangle \right] = \frac{3}{2}k_0 [1 - P(\theta)] \end{aligned} \quad (12)$$

Under LNI and s-polarized light we can define the orientation factor, f_0 , by means [92]:

$$f_0 = \frac{k_y}{k_0} = \frac{3}{4} [1 + P(\theta)] \quad (13)$$

and for a general case, using s- and p- polarized spectra at different incidence angles:

$$P(\theta) = \frac{2k_y - k_z}{2k_y + k_z} \quad (14)$$

For a parallel orientation respect to the x-y plane, $P(\theta) = 1$, being in this case $f_0 = 3/2$ and therefore $k_z = 0$, as for monoaxial films. For a perpendicular orientation respect to the x-y plane $P(\theta) = 0$, and $f_0 = 3/4$ and $2k_y = k_z$. Finally, for a random distribution $P(\theta) = 2/3$, $f_0 = 5/4$ and therefore $2k_y = 5k_z$.

2.2.3. Procedure for obtaining optical parameters: The model described in Scheme 1c contains seven unknown parameters, d_1 , d_2 , n_1 , $n_y = n_x$, n_z , $k_y = k_x$ and k_z . Note the additional difficulty of that actually four of them, n_y , n_z , k_y and k_z , are wavelength-dependent variables. From a purely theoretical perspective, a wide range of experimental measurements of ΔR_p and ΔR_s as a function of α_0 would allow the determination of the model parameters by numerical fitting. However, this information cannot be experimentally accessed using this wide range of measurements due to experimental limitations [74]. These limitations can be overcome by separately measuring (or estimating), of d and n_1 . Thus, d can be determined using ellipsometry at a wavelength without absorption, or by using CPK models, taking into account the molecular area obtained by the compression state of each Langmuir monolayer. On the other hand, the reflection index of the isotropic alkyl chain regions can be assumed as $n_1 = 1.436$ [93].

Spectra with s-polarized light, or under normal incidence are dependent on $n_y = n_x$, and $k_y = k_x$, but not dependent on n_z and k_z . This point might be used to determine n_y , and k_y . Thus, from the LNI spectra we can obtain an approximate k_y value from:

$$k_y \approx \frac{3}{2} \cdot \frac{\lambda \cdot \Delta R_n}{8\pi \cdot d \cdot \sqrt{R_s}} \quad (15)$$

Then n_y , can be obtained applying the Kramers-Krönig relationship [89]

$$n_y(\nu) = n_{y\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{k_y(x) \cdot x}{x^2 - \nu^2} dx \quad (16)$$

Where ν is the frequency. For the application of this equation the k_y values must be extrapolated into the far UV regions, in which those exact values are actually unknown. Starting from this set of n_y values, a new set of k_y values can be obtained through numerical fitting between the experimental and simulated ΔR_n spectra. From the new k_y values a new set of n_y values are obtained by Kramers-Krönig analysis again. These procedures are repeated until the simulated and experimental spectra are identical [89]. The $n_{y\infty}$ value in equation (16) is obtained from the reflection in the absence of absorption.

Finally, n_z and k_z are simultaneously obtained by numerical fitting between the experimental ΔR_p spectra at different incidence angles and the simulated spectra. This procedure will be reviewed below in the application to the behavior of an amphiphilic porphyrin as previously published [79, 80].

2.2.4 Simple analysis criteria: The mathematical treatment described just above is tedious and often is not necessary, especially when the LNI method can be applied (see section 2.1), or if the aim is qualitative information on the orientation of the transition dipoles at the interface. Therefore, it is desirable to have simple criteria allowing determining the approximate orientation of those transition dipoles. To obtain a simple criteria of analysis, the above model is simplified, assuming that the film can be represented by a single layer ($L = 1$) of thickness $d \approx d_1 + d_2$, and optical parameters $n_1 = n_x = n_y = n_z$,

$k_y = k_x$ and k_z . These criteria will be established for constant wavelength, corresponding to the absorption maximum. However, instead of using k_y and k_z , as parameters, we use k_0 and $P(\theta)$. The relationship between these parameters was established in the equations (7) for monoaxial and equation (12) for biaxial degenerated films.

The plot of ΔR vs α_0 for a monoaxial film, being $d = 2$ nm, $n_1 = 1.55$, $k_0 = 0.5$, $P(\theta) = 0.8$ and $\lambda = 500$ nm, is shown in Figure 2. ΔR (ΔR_s , ΔR_p or ΔR_n) represents the difference between the reflection of incoming radiation from the bare air-liquid interface and the Langmuir monolayer-covered air-liquid interface, see Figure 2. Note that reflection is expressed in percentage (%). ΔR_n (%) = 0.509 is obtained using the mentioned values for the parameters, under normal incidence.

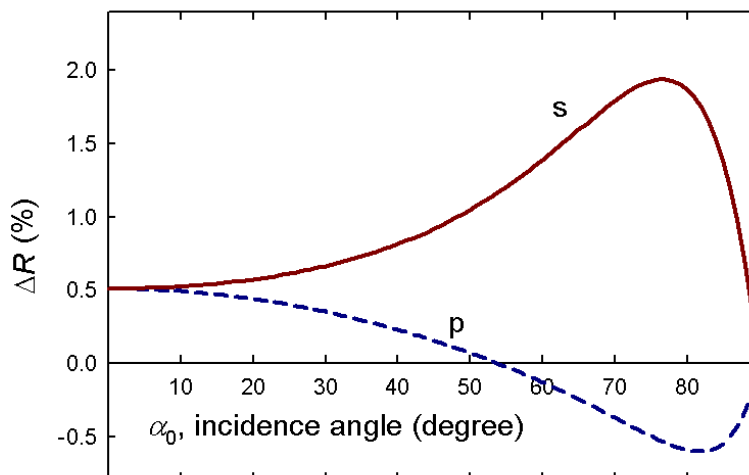


Figure 2 Plot of ΔR_s (solid red) and ΔR_p (dashed blue) vs α_0 , for a monoaxial film, being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$, $P(\theta) = 0.8$, and $\lambda = 500$ nm [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

ΔR_s (red solid line, Figure 2) is always positive for the considered set of parameters. ΔR_s is higher than ΔR_n except for angles close to 90° . ΔR_p (blue dashed line, Figure 2) is lower than ΔR_n , not being always the case as discussed below. ΔR_p can be either positive or negative. The existence of negative bands, as in IRRAS [76, 77], takes place exclusively for p-polarized light with very thin films and for incidence angles near or higher than the Brewster angle, i. e., 53.15° for air-water interface. In this scenario and depending on the experimental conditions, the reflection of incident light from the Langmuir monolayer at the air-liquid interface might be lower than the bare air-liquid interface. This phenomenon is quite sensitive to the optical properties of the Langmuir monolayer.

Both ΔR_s and ΔR_n show dependence on $k_x = k_y$, i. e. the absorption constant on the x-y plane. Note that ΔR_s and ΔR_n do not depend on k_0 and $P(\theta)$ separately. $\Delta R_s/\Delta R_n$ values versus α_0 for $\lambda = 500$ nm ($d = 2$ nm, $n_1 = 1.55$, $k_0 = 0.5$, and different $P(\theta)$ values) are shown in Figure 3 and 4, for monoaxial and biaxials films, respectively. The plot of $\Delta R_s/\Delta R_n$ allows the direct comparison of the different plots. The plot of $\Delta R_s/\Delta R_n$ is almost independent of $P(\theta)$ value, see Figures 3a and 4, indicating that the curves do not offer information about of the dipoles orientation, but only of the in-plane component of the dipole.

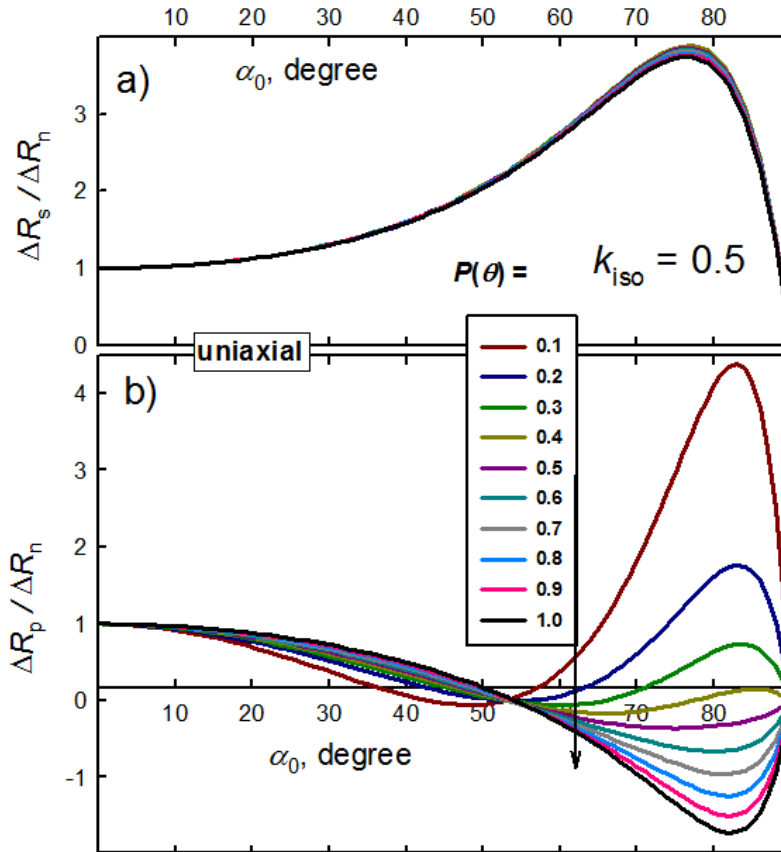


Figure 3 a) Plot of $\Delta R_s / \Delta R_n$ and b) $\Delta R_p / \Delta R_n$ vs α_0 , being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm for a monoaxial film. The different $P(\theta)$ values are indicated in the Figure [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

The variation of $\Delta R_p / \Delta R_n$ vs α_0 assuming the same conditions as above are shown in Figure 3b (monoaxial) and 4 (biaxial). For monoaxial films (Figure 3b), and for incidence angles higher than the Brewster angle, the $\Delta R_p / \Delta R_n$ relationship is positive or negative as a function of $P(\theta)$. The maximum of variation is observed at $\alpha_0 \approx 83^\circ$, although for $\alpha_0 = 70^\circ$, the variation is wide enough to define appropriate criteria analysis. Figure 3

clearly shows the enormous potential of the UVRAS, given that either positive or negative bands are obtained based solely on the transition dipole tilt of the chromophores at the air-liquid interface. For biaxial films (Figure 4) the $\Delta R_p/\Delta R_n$ vs α_0 plot is practically independent of the $P(\theta)$ values, except for $\alpha_0 > 65$, which can be used to define analysis criteria.

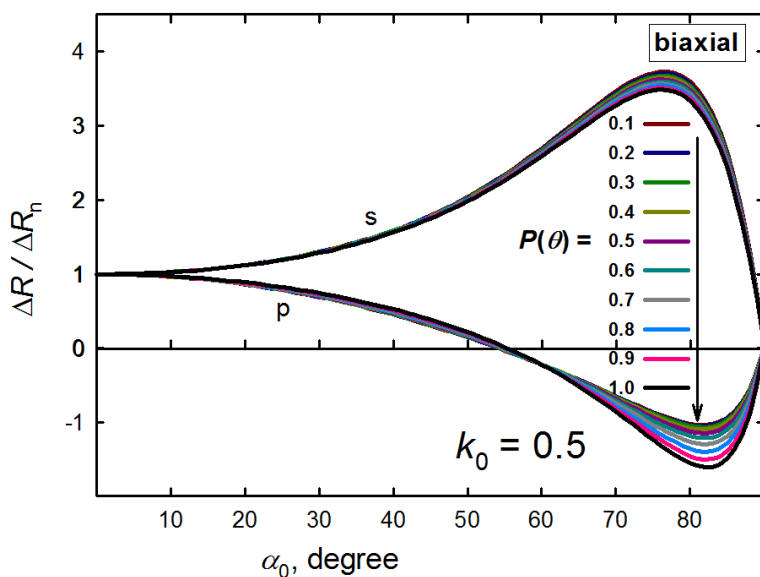


Figure 4 Plot of $\Delta R_s/\Delta R_n$ and $\Delta R_p/\Delta R_n$ vs α_0 , being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm for a biaxial degenerated film. The different $P(\theta)$ values are indicated. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

The dichroic relationship $\Delta R_s/\Delta R_p$ could be used as criteria analysis for obtaining approximate $P(\theta)$ values. However, for uniaxial films ΔR_p may be zero, so it is convenient to use in this case the inverse relationship $\Delta R_p/\Delta R_s$. Figure 5 shows the representation $\Delta R_p/\Delta R_s$ vs $P(\theta)$ for monoaxial films, being $k_0 = 0.5$, under different incidence angles.

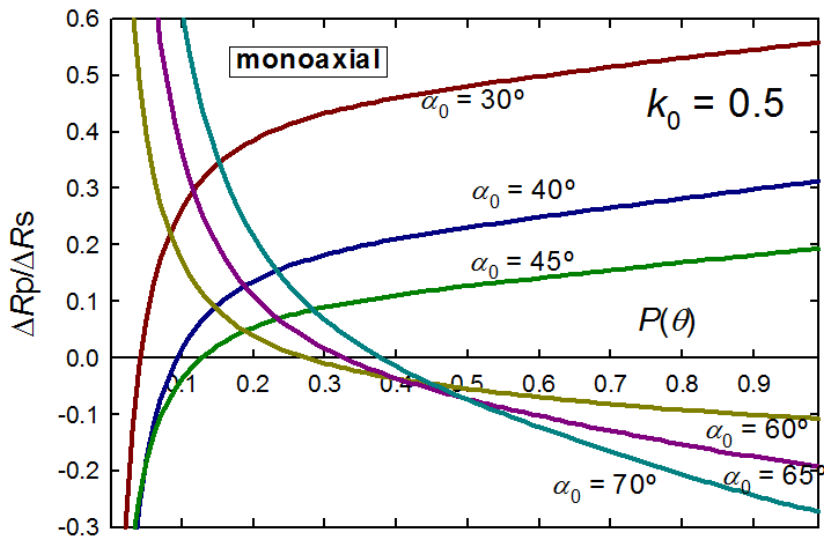


Figure 5 Plot of $\Delta R_p / \Delta R_s$ vs $P(\theta)$, for monoaxial films being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm. The different incidence angles values, α_0 , are indicated in the Figure [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

For biaxial degenerated films, the $\Delta R_s / \Delta R_p$ vs $P(\theta)$ representation is shown in Figure 6. In this case, the dichroic relationship is expressed as $\Delta R_s / \Delta R_p$. For $\alpha_0 \leq 60^\circ$, the curves show little variation and cannot be used to estimate $P(\theta)$.

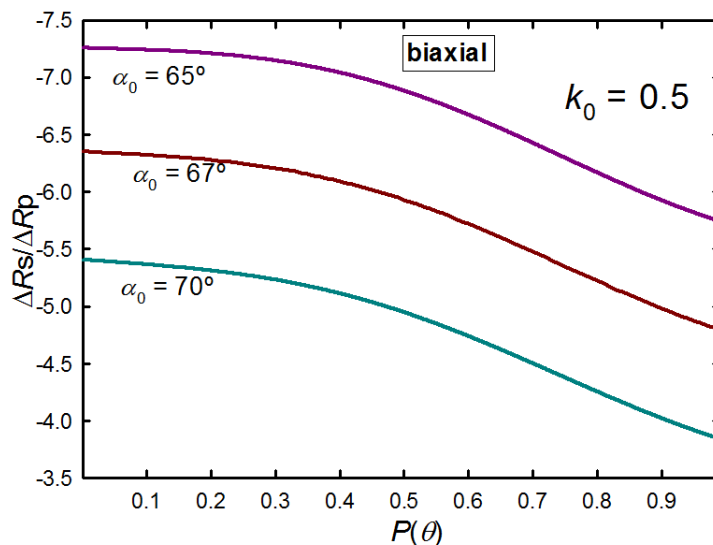


Figure 6 Plot of $\Delta R_s/\Delta R_p$ vs $P(\theta)$, for biaxial degenerated films, being $d = 2$ nm, $n_1 = 1.55$, $k_{\text{iso}} = 0.5$ and $\lambda = 500$ nm. The different incidence angles values, α_0 , are indicated in the Figure. [74] Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

The curves shown in Figures 5 and 6, depend on the absolute value of k_0 , d , and n_1 , and therefore cannot be used in a general manner. However, the relationship $\Delta R_p/\Delta R_s$, is approximately coincident with those shown in Figures 5 and 6, under the conditions: $d \leq 3$ nm and $1.75 \geq n_1 \geq 1.45$, and leads to errors in the estimation of $P(\theta)$ which are at most 10% when used for k_0 values in the range of $1.5 \geq k_0 \geq 0.05$. These values are typical in Langmuir monolayers. As previously commented, the curves shown in Figures 5-6 offer only an approximate value of $P(\theta)$. More accurate values require the application of the procedure described in section 2.2.3.

In summary, we have introduced in great detail the theoretical framework and the equations required for a successful data treatment of UVRAS data for any Langmuir monolayer. In the spirit of illustrating the

usage of this procedure for the data treatment, we describe the application of such treatment to a published study from our group [79, 80] in the following section.

3. AGGREGATION OF A SULFONATED AMPHIPHILIC PORPHYRIN AT THE AIR–WATER INTERFACE.

Once reviewed the theoretical and experimental framework for the application of the UVRAS technique by our and other groups, we devote this section to review in detail the application of the data treatment to a previously published example. This study is of great interest in this sense, given a porphyrinoid group was successfully aggregated at the air-water interface [79, 80] Porphyrins with D_{4h} symmetry show a sharp degenerate band around 420 nm (Soret band) [81]. J- and H-aggregation of the porphyrins are detected through spectrum changes of this degenerated band. However, sometimes degeneration is removed due to a dense packing of the porphyrins at the air-liquid interface, and a splitting of the Soret band is detected [82-84].

Inset in Fig. 7 the π -A isotherms of $(OD)_3TPPS_3$ on a basic subphase (pH 11, NaOH) is shown, according to previous studies by our group [79, 80]. The UVRAS spectra under normal incidence (ΔR_n) are shown in Figure 7, at different surface pressures. At large molecular areas (i.e. $A > 8 \text{ nm}^2$), the Soret band maximum appears at 422 nm, which is close to the maximum absorption peak in bulk solution with methanol as a solvent (ca. 417 nm), thus indicating the non-aggregated state of the porphyrin at this molecular area [79]. Under

compression, the intensity of the band increases, and the position of the maximum shifts to longer wavelengths (i.e. 427 nm), thereby retaining this behavior in the area region from 3 to 1.5 nm². The red shift of the Soret band can be assigned to J-aggregate formation. Upon further increase of the surface pressure, the Soret band intensity decreases and its maximum is red-shifted to 430 nm, simultaneously with the emergence of a new band at 405 nm (see Figure 7). Remarkably, this phenomenon is reversible during the expansion–compression cycles [79]. The appearance of these two bands (430 and 405 nm) was interpreted as due to the broken of degeneracy and consequent splitting of the Soret band. In fact, the transmission spectra the (OD)₃TPPS₃ monolayers transferred onto solid substrate, at a surface pressure of 30 mN/m, showed polarization dependence when s and p polarization light was used [79]. We review here the use of UVRAS under LVI to verify this phenomenon in situ on the air-water interface.

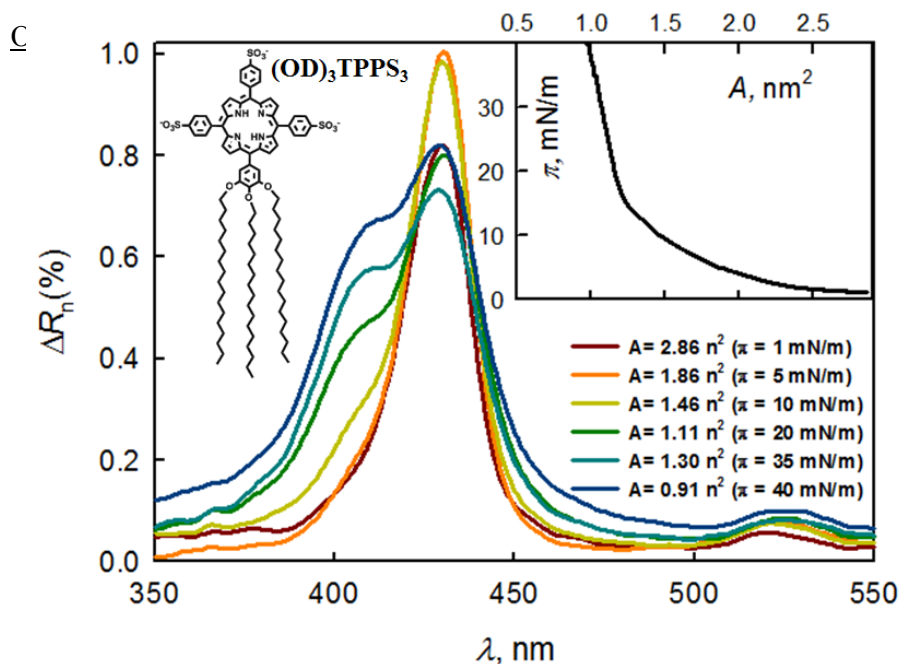


Figure 7 UVRAS under LNI (ΔR_n) of $(\text{OD})_3\text{TPPS}_3$ monolayers on the basic aqueous subphase ($\text{pH}=11$) at different surface pressures. Inset left: Surface pressure - area (π - A) isotherm of $(\text{OD})_3\text{TPPS}_3$ monolayers. Inset right: $(\text{OD})_3\text{TPPS}_3$ molecular structure [79]. Copyright from Wiley-VCH, 2008.

3.1 Reflection at low surface pressure: Selected reflection spectra from our previous study at $\pi = 1\text{mN/m}$ ($A=2.86\text{ nm}^2$) using p- polarized light at variable incidence angle are shown in Figure 8 (continuous line). The UVRAS spectrum under normal incidence has been also included for comparison (light blue continuous line). The shape of the bands does not show variation for the different spectra, also for s polarization (data not shown). Only in the case of p polarization and incidence angles close to the Brewster angle of the air-water interface (53.15°) a variation is observed, which can be interpreted as a optical effect [75]. Therefore, the band can be ascribed to a single absorption mode, and thus the Soret band degeneration must be preserved. For a incidence angle of $\alpha_0 = 67^\circ$, $\Delta R_s/\Delta R_p \approx 4.9$ (data not show), allowing to obtain, from Figure 6 that $P(\theta) \approx 0.95$.

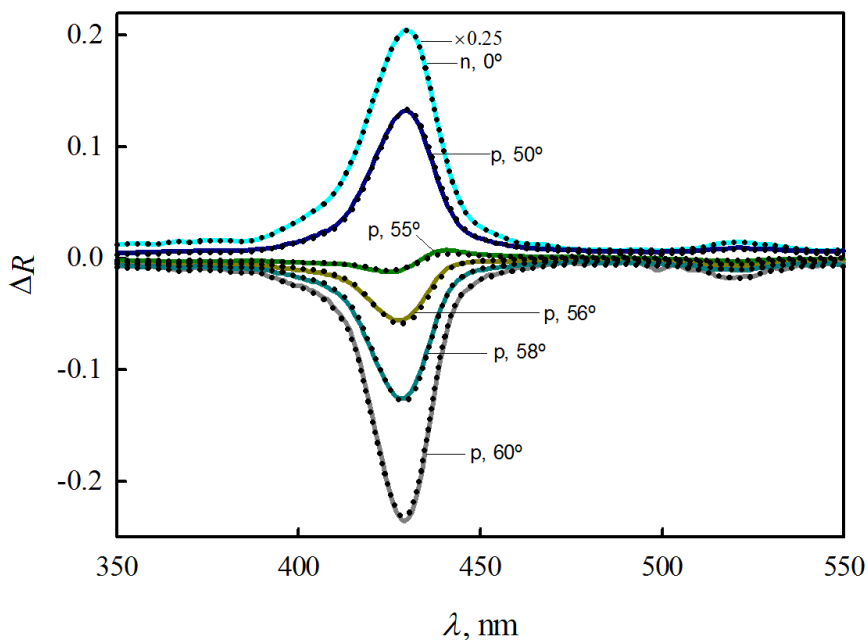


Figure 8 Continuous line: UVRAS under LVI using p polarized radiation (ΔR_p) of $(\text{OD})_3\text{TPPS}_3$ monolayers at $\pi = 1\text{mN/m}$ ($A=2.86\text{ nm}^2$). The incidence angle is indicated in the figure. For comparison the spectrum obtained under LNI is included multiplied by 0.25 (light blue continuous line). Others conditions as in Figure 7. Dots: simulated spectra at different incidence angle by using the optical parameters shown in Figure 9 [79, 80].

The optical parameters of the $(\text{OD})_3\text{TPPS}_3$ Langmuir monolayer can be obtained by the numerical procedure described in the section 2.2.3. The value of thickness of this monolayer is required for such calculation. For our previous study, the thickness of the $(\text{OD})_3\text{TPPS}_3$ Langmuir monolayer is $d = 3.35\text{ nm}$ (ellipsometry data) at a value of molecular area of $A=0.9\text{ nm}^2$ (π ca. 35 mN/m) [80]. Using ellipsometry parameters from a previous study[80] the thickness is of the monolayer is calculated to be ca. 1.2 nm for $A=2.8\text{ nm}^2$ ($\pi \approx 1\text{mN/m}$). Given the large tilting of the $(\text{OD})_3\text{TPPS}_3$ molecules at low values of surface pressure, the consideration of the two separated regions as hydrophobic regions (alkyl chains) and hydrophilic (polar group) of the

monolayer is not possible, as in Scheme 1. Thus, in this case we assume that the monolayer can be represented by a single layer of average constant optical parameters. The obtained optical parameters (n_q and k_q) are shown in Figure 9. Note that $k_z \approx 0$ for any wavelength, indicating an almost planar orientation of the porphyrin ring with respect to the air-liquid interface. $P(\theta)$ values obtained from equation (14) are displayed as a yellow line. Close to the maxima of the wavelength, $P(\theta)$ is close to the unity, as expected from previous considerations.

The calculated spectra at different incidence angle are displayed as black dots in Figure 8. There is a good agreement between experimental and simulated results.

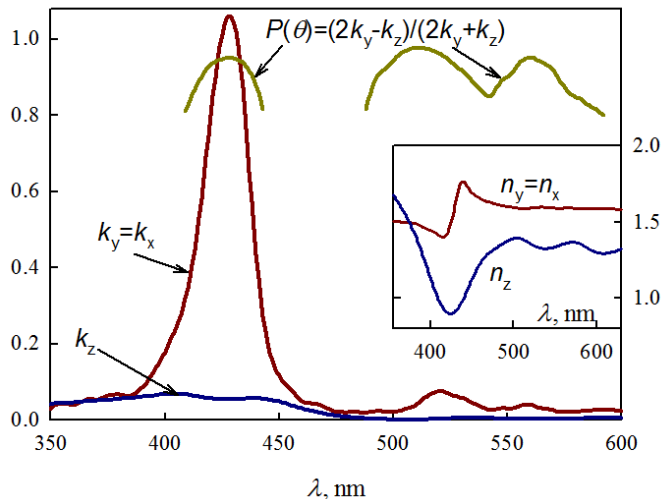


Figure 9 Optical parameters for the $(OD)_3TPPS_3$ monolayers at $\pi = 1\text{mN/m}$ ($A=2.86\text{ nm}^2$). Plot of $k_y=k_x$ (red line), k_z (blue line) and $P(\theta)$ (yellow line) vs wavelength (λ). Inset: Plot of $n_x=n_y$ (red line) and n_z (blue line) vs λ .

3.2 Reflection at high surface pressure: Selected UVRAS spectra at $\pi = 35$ mN/m ($A=0.9$ nm²) using p- polarized light at variable incidence angle are shown in Figure 10 (continuous line). For comparison, the spectrum made under normal incidence (light blue continuous line) is also shown. For n and p polarization light with an incidence angle lower than the Brewster angle, two bands could be observed at 430 and 405 nm. The shape of the spectra remains identical when s polarized radiation was used (data not shown). When we used p polarized light and incidence angles above the Brewster angle, the 430 and 405 nm bands are observed, obtaining a negative ΔR . However, a new positive peak is observed at ca. 380 nm. The appearance of positive peaks using p polarization and incidence angle above the angle Brewster is not feasible for biaxial degenerate absorption mode (see Figure 4), so that the only explanation of this phenomenon is the breaking of the degeneracy of the solet band, as previously proposed [79].

For a incidence angle of $\alpha_0 = 60^\circ$, $\Delta R_p/\Delta R_s$ are -0.09, -0.10 and +0.06, at 430, 409 and 380 nm respectively. Thus, a preliminary estimation of $P(\theta)$ from Figure 5 can be done. However, the overlap of the bands makes this procedure inaccurate.

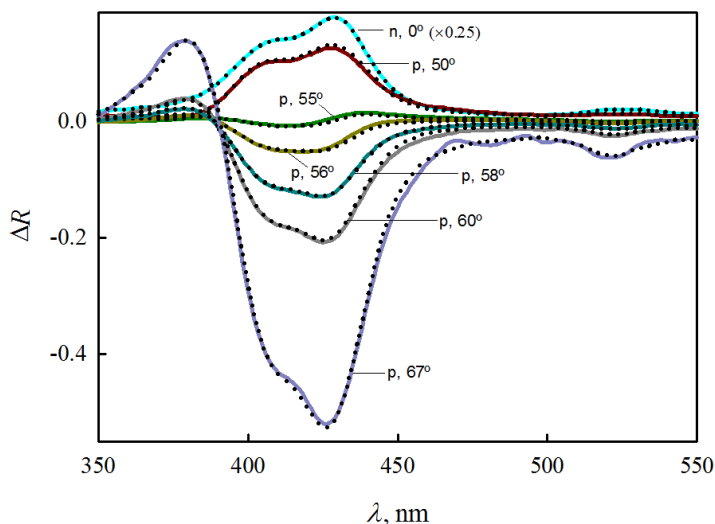


Figure 10 Continuous line: UVRAS under LVI using p polarized radiation (ΔR_p) of $(OD)_3TPPS_3$ monolayers at $\pi = 35\text{mN/m}$ ($A=0.9\text{ nm}^2$). The incidence angle is indicated in the figure. For comparison the spectrum obtained under LNI is included multiplied by 0.25 (light blue continuous line). Others conditions as in Figure 7. Dots: simulated spectra at different incidence angle by using the optical parameters shown in Figure 11 [79, 80].

Starting from the previous set of parameters of $d = 3.35\text{ nm}$, $A=0.9\text{ nm}^2$ [80] and using space filling CPK models, the estimation of the thickness of the $(OD)_3TPPS_3$ molecule for a completely vertical configuration is 4.2 nm (1.9 nm for the porphyrin group and 2.3 nm for the alkyl chains). The tilt of the $(OD)_3TPPS_3$ molecule with respect to the air-water interface is thus influencing this result. Assuming a vertical packing at a molecular area of 0.9 nm^2 , the thickness of the polar layer is $d_2 = 1.9\text{ nm}$ (see Scheme 1). Considering that the minimal area for the alkyl chains is ca. 0.6 nm^2 , then the average tilt for the alkyl chain is $\text{acos}(0.60/0.90)$ ca. 48° , and thus the thickness for the alkyl chains region should be $d_1 = 2.3\text{cos}(48^\circ) = 1.5\text{ nm}$. Therefore, the overall thickness at $A = 0.9\text{ nm}^2$ should be $d = d_1 + d_2 = 3.4\text{ nm}$,

which is in good agreement with the value previously estimated from ellipsometry.

Figure 11 shows the optical parameters obtained (n_q and k_q) under the previous considerations. These parameters were used to calculate the spectra shown in Figure 10 (black dots). A good coincidence between experimental and simulated results was obtained. k_y shows two peaks as 430 and 405 nm, whereas k_z shows only a peak at ca. 380 nm. However, while the 430 nm peak is present only in the x-y component, small contributions of the 380 nm peak on the x-y component and of the 405 nm peaks on the z component might be present as well (see Figure 11). The yellow line in Figure 11 show the $P(\theta)$ values obtained from equation (9). $P(\theta)$ values of ca. 0.99, 0.95 and 0.51 at 430, 405 and 380 nm respectively, were obtained. However, given the overlap of the peaks, the $P(\theta)$ values correspond to average values originated by the different absorption modes. For monoaxial components and overlapping between the absorption modes equation (7) can be expressed as:

$$\begin{aligned} k_x = k_y &= \frac{3}{2} \sum_i k_{0,i} P(\theta_i) \\ k_z &= 3 \sum_i k_{0,i} [1 - P(\theta_i)] \end{aligned} \quad (17)$$

where $k_{0,i}$ are the different isotropic absorption constants, and $P(\theta)$ the corresponding order parameter for each absorption mode i . We can obtain the maximum isotropic absorption constant, k_{\max} , from

$$k_{\max} = k_x + k_y + k_z = 3 \sum_i k_{0,i} \quad (18)$$

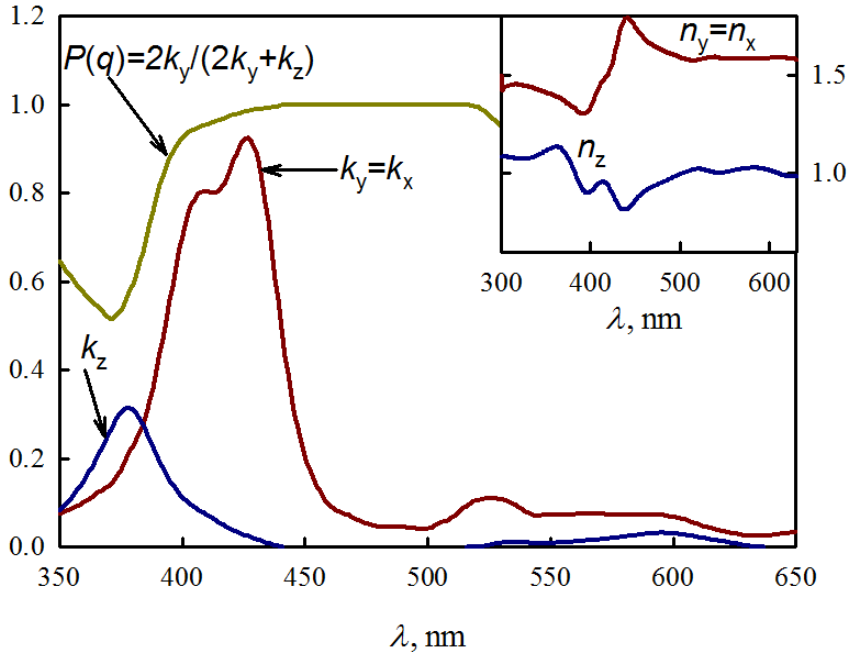


Figure 11 Optical parameters for the $(OD)_3TPPS_3$ monolayers at $A=0.9 \text{ nm}^2$ ($\pi \approx 35\text{mN/m}$). Plot of $k_y = k_x$ (red line), k_z (blue line) and $P(\theta)$ (yellow line) vs wavelength (λ). Inset: Plot of $n_x = n_y$ (red line) and n_z (blue line) vs λ .

This expression is valid for degenerated biaxial absorption modes, also. Figure 12-a (black line) show the k_{max} values in the 330-450 nm regions. Lorentzian asymmetric functions were used for modeling k_{max} . The numerical fitting requires a minimum of 4 peaks ($k_{0,i}$ absorption modes), being plotted in Figure 12-a at 368 nm (gray line, $3k_{0,1}$), 378 nm (green line, $3k_{0,2}$), 404 nm (yellow line, $3k_{0,3}$) and 429 nm (cyan line, $3k_{0,4}$).

Given the $k_{0,i}(\lambda)$ values, the order parameters, $P(\theta)$, of each absorption mode can be obtained by numerical fitting of $k_y = k_x$ and k_z . (see Figure 11) to equations (17). Thus, we obtain that $P(\theta) = 0.82, 0.09, 0.99$ and 1.00 , for the 368, 378, 404 and 429 nm absorbing modes, respectively.

Figures 12b and 12c show the $k_y = k_x$ (red line, Figure 12b) and k_z (blue line, Figure 12c) values. Moreover, Figure 12b show the different contributions of the 4 absorption modes in the way $(3/2)k_{0,i}P(\theta_i)$, see equation (17). In Figure 12c the different contributions are shown in the way $3k_{0,i}[1-P(\theta_i)]$, see equation (17). Three of the absorption modes are almost parallel to the interface (368, 404 and 429 nm), mainly contributing to the $k_y = k_x$ components (Figure 12b). The 378 nm absorption mode (green line) is almost perpendicular at the interface ($P(\theta) = 0.09$), mainly contributing to the k_z component (Figure 12c).

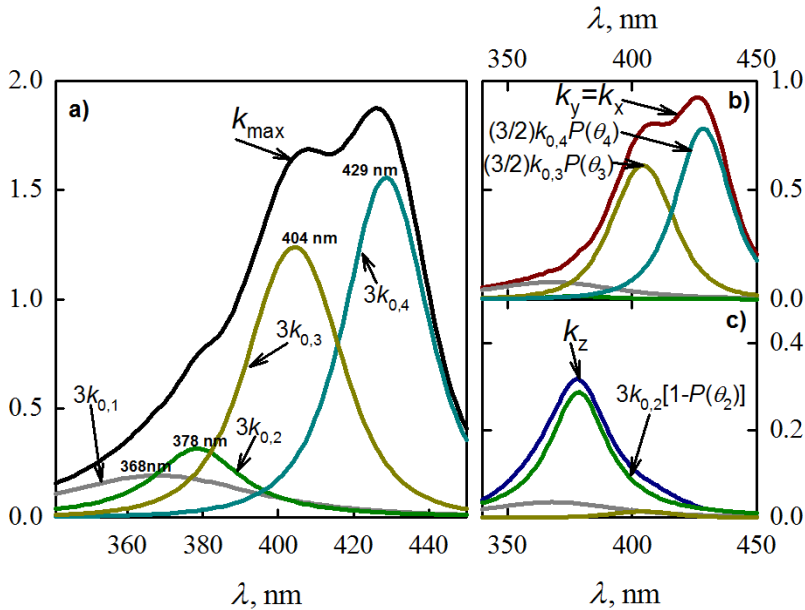


Figure 12 a) Plot of $k_{\max} = 2k_y + k_z$ (black line), b) $k_y = k_x$ (red line), and c) k_z (blue line) vs λ . The gray line (368 nm), green line (378 nm), yellow line (404 nm) and cyan line (429 nm) represent the different absorption modes contributions, as $3k_{0,i}$ in a), as $(3/2)k_{0,i}P(\theta_i)$ in b), and as $3k_{0,i}[1-P(\theta_i)]$ in c) [79, 80].

We emphasize that the 378 nm peak has not been detected by any transmission techniques, including linear dichroism at different incidence angles [79, 80]. The results from our previous study and reviewed in this section (Figures 10-12) show the enormous potential of the UVRAS technique for solving absorption peaks with different polarizations. In addition, our results have opened a new interpretation of the Soret band splitting of the $(\text{OD})_3\text{TPPS}_3$. Previously the Soret band splitting was related with the 430 and 405 nm bands. However, according to UVRAS spectra under LVI, two types of porphyrin aggregates seem to appear; a) J-type aggregates responsible for the 430 nm band, where Soret band degeneration is preserved, b) a second type of aggregates with a strong exciton-coupling, resulting in the Soret band splitting, which originates peaks at 405 and 378 nm. The 405 and 430 nm peaks are almost parallel to the interface, whereas the 378 nm peak is weaker and almost normal to the interface, therefore it cannot be detected by transmission spectroscopy.

5. CONCLUSIONS

The UV-Visible Reflection-Absorption Spectroscopy (UVRAS) technique has been reviewed, highlighting the wide range of applications for studying ultrathin films. This technique developed by D. Möbius et al. in the mid-80s [1-3], was initially referred as UV-Visible Reflection Spectroscopy. In spite of the enormous potential of this technique, the applications of the UVRAS have been limited mainly to reflection measurements under light

normal incidence. Only recently, UVRAS measurements have been extended to different incidence angles with s- and p- polarized radiation [74]. UVRAS is formally identical to IR reflection-absorption spectroscopy (IRRAS)) on semi-transparent substrates [75-78]. Therefore, all the methodology developed for this IR technique can be applied in UV-visible region. UVRAS can be applied to air-solid or air-liquid interfaces. Langmuir monolayers and the application of UVRAS to studies at the air-liquid interface has been the object of this review. UVRAS produces positive or negative bands when p-polarized radiation is used, depending on the incidence angle and the orientation of dipole absorption [74], as is the case of IRRAS [75]. UVRAS technique provides highly valuable information on tilt of chromophores at the interface. Thus, the dichroic relationship $\Delta R_s/\Delta R_p$ can be used as semiquantitative criteria analysis for obtaining the parameter order, $P(\theta)$, for monoaxial, or biaxial degenerates absorption modes. However, for obtaining this order parameter in a general way, the optical parameters of the film must be determined by numerical fitting, which allowed simulates the experimental spectra very accurately.

To illustrate the huge potential of the UVRAS technique, the splitting of the Soret band of an amphiphilic porphyrin at the air-water as previously reported by our group has been reviewed. In such case, a peak at 375nm at high incidence angle and using p polarized radiation was successfully characterized. Remarkably, that peak could not be detected by any

transmission spectroscopy techniques, including linear dichroism, given the absorption mode is weaker and almost normal to the air-water interface.

OUTLOOK

Despite the great popularity that has reached IRRAS technique as routine technique in many research laboratories, UVRAS has surprisingly not drawn much attention.

In the recent years, new developments in reflection and absorption linear optical techniques have been employed not only for characterization of self-assembled nanomaterials, but also for the determination of the nanomaterials optical parameters or the construction of innovative devices and sensors.

UVRAS can be applied to the study of ultrathin films, (also referred as nanolayers) formed from a wide range of organic and inorganic materials at a given interface. Such interfaces comprise, for example; air-solid, air-liquid, liquid-liquid or liquid-solid. These films play an important role in many research and technology areas, such as optoelectronics, bioscience, flotation, sorbents, pigments, protective and passivating coatings, sensors and others system with applications in nanotechnology, which includes the synthesis–deposition and characterization of ultrathin films with a prescribed composition, morphology–architecture and thicknesses on the nm order. We therefore expect this review provides a comprehensive guide to the usage of the highly valuable UVRAS technique.

APPENDIX

The anisotropic thin film is assumed to be material with thickness d , located between two isotropic transparent media of infinite thickness, air and water in our case. The film could be discomposed in L anisotropy biaxial stratified layers of thickness d_j (see Scheme 2) [89]. The anisotropic complex index N_{jk} is defined by:

$$N_{jq} = n_{jq} + i \cdot k_{jq}$$

Where i , is the imaginary number, n_{jq} is the refractive index, k_{jq} is the absorption constant, j represent the j th layer, and q , the x , y or z axis.

Moreover:

$$\hat{\alpha}_{js} = \sin^{-1} \left(\frac{N_0}{N_{jy}} \sin(\alpha_0) \right)$$

$$\hat{\alpha}_{jp} = \sin^{-1} \left(\frac{N_0}{N_{jz}} \sin(\alpha_0) \right)$$

$$\alpha_w = \sin^{-1} \left(\frac{N_0}{N_w} \sin(\alpha_0) \right)$$

Where α_0 is the incidence angle, $N_0 = 1$ and $N_w = 1.33$, are the refractive index of the air and water environments, and s and p , represent the light polarization. Next we can define:

$$g_{js} = N_{jy} \cos(\hat{\alpha}_{js}) \quad g_{jp} = \frac{\cos(\hat{\alpha}_{jp})}{N_{jx}}$$

$$g_0 = N_0 \cos(\alpha_0) \quad g_w = N_w \cos(\alpha_w)$$

$$\beta_{js} = \frac{2\pi d_j N_{jy}}{\lambda} \cos(\hat{\alpha}_{js})$$

$$\beta_{jp} = \frac{2\pi d_j N_{jx}}{\lambda} \cos(\hat{\alpha}_{jp})$$

Using these definitions we can evaluate

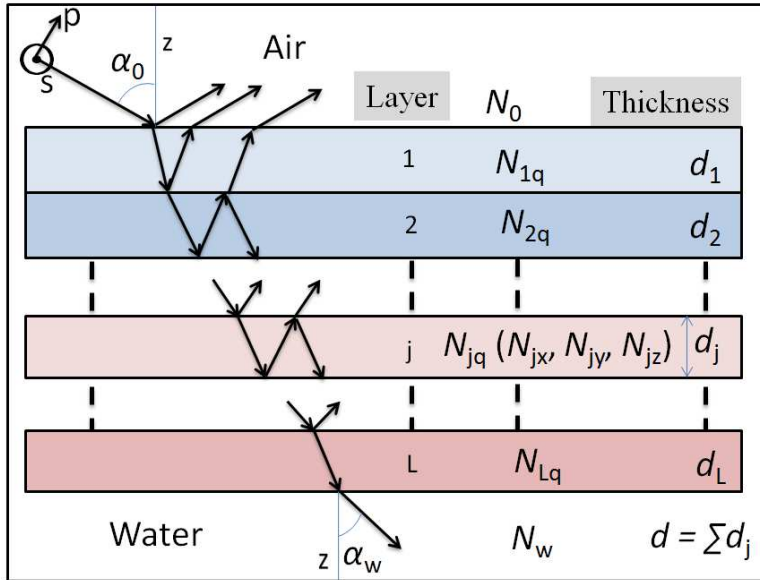
$$Ms = \prod_{j=1}^L \begin{pmatrix} \cos(\beta_{js}) & -i \cdot \frac{\sin(\beta_{js})}{g_{js}} \\ -i \cdot g_{js} \sin(\beta_{js}) & c \cos(\beta_{js}) \end{pmatrix} \quad Mp = \prod_{j=1}^L \begin{pmatrix} \cos(\beta_{jp}) & -i \cdot \frac{\sin(\beta_{jp})}{g_{jp}} \\ -i \cdot g_{jp} \sin(\beta_{jp}) & c \cos(\beta_{jp}) \end{pmatrix}$$

We obtain the reflectance R_s and R_p as follows:

$$rs = \frac{(Ms_{0,0} + Ms_{0,1} \cdot g_w) g_0 - (Ms_{1,0} + Ms_{1,1} \cdot g_w)}{(Ms_{0,0} + Ms_{0,1} \cdot g_w) g_0 + (Ms_{1,0} + Ms_{1,1} \cdot g_w)}$$

$$rp = \frac{(Mp_{0,0} + Mp_{0,1} \cdot g_w) g_0 - (Mp_{1,0} + Mp_{1,1} \cdot g_w)}{(Mp_{0,0} + Mp_{0,1} \cdot g_w) g_0 + (Mp_{1,0} + Mp_{1,1} \cdot g_w)}$$

$$R_s = (|rs|)^2 \quad R_p = (|rp|)^2$$



Scheme 2: Optical configuration of the stratified layers film.

ACKNOWLEDGEMENTS

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GRAPHICAL ABSTRACT

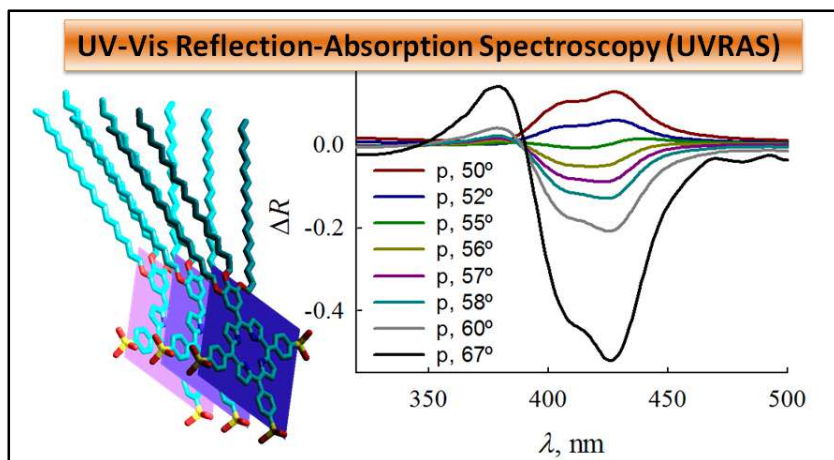


FIGURE CAPTIONS

Figure 1 A) A Langmuir monolayer of an organometallic oligo(phenylene)ethynylene derivative was studied by UV-vis reflection spectroscopy. Based on the knowledge of the intermolecular interactions at the air-water interface, the behavior of this layer once transferred to a solid support show features of molecular wires [47]. Copyright from American Chemical Society, 2015. B) Langmuir monolayers of a tetrapyrrolyl-substituted porphyrin have shown a large selectivity in sensing Cu^{2+} toward Hg^{2+} ions present in the subphase. UV-vis reflection spectroscopy provided unique experimental evidence on the detailed interaction of the metallic ions with the porphyrin; whereas Hg^{2+} ions interact with both the pyridyl substituents and the central bite of the ring inducing H-aggregation, Cu^{2+} ions interact with only the porphyrin peripheral substituents. This highly detailed information on intermolecular interactions is most valuable when designing sensing devices [52]. Copyright from American Chemical Society, 2014.

Scheme 1 Schematic illustration for the coordinate definitions for the transition dipole in the case of a) monoaxial and b) biaxial degenerated films. c) Sketch of the reflection and transmission in an ideal Langmuir film divided in two layers.

Figure 2 Plot of ΔR_s (solid red) and ΔR_p (dashed blue) vs α_0 , for a monoaxial film, being $d = 2 \text{ nm}$, $n_1 = 1.55$, $k_{\text{iso}} = 0.5$, $P(\theta) = 0.8$, and $\lambda = 500 \text{ nm}$ [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

Figure 3 a) Plot of $\Delta R_s/\Delta R_n$ and b) $\Delta R_p/\Delta R_n$ vs α_0 , being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm for a monoaxial film. The different $P(\theta)$ values are indicated in the Figure [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

Figure 4 Plot of $\Delta R_s/\Delta R_n$ and $\Delta R_p/\Delta R_n$ vs α_0 , being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm for a biaxial degenerated film. The different $P(\theta)$ values are indicated. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

Figure 5 Plot of $\Delta R_p/\Delta R_s$ vs $P(\theta)$, for monoaxial films being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm. The different incidence angles values, α_0 , are indicated in the Figure [74]. Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

Figure 6 Plot of $\Delta R_s/\Delta R_p$ vs $P(\theta)$, for biaxial degenerated films, being $d = 2$ nm, $n_1 = 1.55$, $k_{iso} = 0.5$ and $\lambda = 500$ nm. The different incidence angles values, α_0 , are indicated in the Figure. [74] Reproduced from Ref. 74 with permission from the PCCP Owner Societies.

Figure 7 UVRAS under LNI (ΔR_n) of $(OD)_3TPPS_3$ monolayers on the basic aqueous subphase (pH=11) at different surface pressures. Inset left: Surface pressure - area ($\pi - A$) isotherm of $(OD)_3TPPS_3$ monolayers. Inset right: $(OD)_3TPPS_3$ molecular structure [79]. Copyright from Wiley-VCH, 2008.

Figure 8 Continuous line: UVRAS under LVI using p polarized radiation (ΔR_p) of $(OD)_3TPPS_3$ monolayers at $\pi = 1$ mN/m ($A=2.86$ nm²). The incidence angle is indicated in the figure. For comparison the spectrum obtained under LNI is included multiplied by 0.25 (light blue continuous line). Others conditions as in Figure 7. Dots: simulated spectra at different incidence angle by using the optical parameters shown in Figure 9 [79, 80].

Figure 9 Optical parameters for the $(OD)_3TPPS_3$ monolayers at $\pi = 1$ mN/m ($A=2.86$ nm²). Plot of $k_y = k_x$ (red line), k_z (blue line) and $P(\theta)$ (yellow line) vs wavelength (λ). Inset: Plot of $n_x = n_y$ (red line) and n_z (blue line) vs λ .

Figure 10 Continuous line: UVRAS under LVI using p polarized radiation (ΔR_p) of $(OD)_3TPPS_3$ monolayers at $\pi = 35$ mN/m ($A=0.9$ nm²). The incidence angle is indicated in the figure. For comparison the spectrum obtained under LNI is included multiplied by 0.25 (light blue continuous line). Others conditions as in Figure 7. Dots: simulated spectra at different incidence angle by using the optical parameters shown in Figure 11 [79, 80].

Figure 11 Optical parameters for the $(\text{OD})_3\text{TPPS}_3$ monolayers at $A=0.9 \text{ nm}^2$ ($\pi \approx 35\text{mN/m}$). Plot of $k_y = k_x$ (red line), k_z (blue line) and $P(\theta)$ (yellow line) vs wavelength (λ). Inset: Plot of $n_x = n_y$ (red line) and n_z (blue line) vs λ .

Figure 12 a) Plot of $k_{\text{max}} = 2k_y + k_z$ (black line), b) $k_y = k_x$ (red line), and c) k_z (blue line) vs λ . The gray line (368 nm), green line (378 nm), yellow line (404 nm) and cyan line (429 nm) represent the different absorption modes contributions, as $3k_{0,i}$ in a), as $(3/2)k_{0,i} P(\theta)$ in b), and as $3k_{0,i} [1-P(\theta)]$ in c) [79, 80].

Anexo



La Tesis Doctoral presentada por D. Carlos María Rubia Payá que lleva por título “Estudio de la Agregación de Colorantes en Películas Mixtas Ultrafinas” consta de los siguientes apartados:

Objetivos, Introducción, Resultados y Discusión, Conclusiones, Resumen y Anexo.

Se pretende su defensa como compendio de publicaciones en base a que se cumplen los requisitos establecidos para ello, como se documenta a continuación:

Publicaciones de la Tesis Doctoral:

- From Two-Dimensional to Three-Dimensional at the Air/Water Interface:

The Self-Aggregation of the Acridine Dye in Mixed Monolayers

Carlos Rubia-Paya, Eugenio Jiménez-Millan, Juan J. Giner-Casares, Gerald Brezesinski, María Teresa Martín-Romero, and Luis Camacho

Langmuir. **2013**, 29, 4796-4805

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- 2D Chiral Structures in Quinoline Mixed Langmuir Monolayers

Carlos Rubia-Payá, J.J. Giner-Casares, M.T. Martín-Romero, D. Möbius and Luis Camacho

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Otras Publicaciones derivadas de esta Tesis

- "Control of the Lateral Organization in Langmuir Mono layers via Molecular Aggregation of Dyes"

Gonzalez-Delgado, AM; **Rubia-Paya, C**; Roldan-Carmona, C; Giner-Casares, JJ; Perez-Morales, M; Munoz, E; Martin-Romero, MT; Camacho, L; Brezesinski, G

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Comunicaciones y Ponencias en Congresos:

- Autores: Carlos Rubia Payá, J.J. Giner Casares, Gustavo de Miguel, M.T.

Martín Romero, D. Möbius and Luis Camacho

Título: Morphological and Structural Study of an Amphiphilic Cyanine forming Langmuir Monolayers

Congreso: 15 th Internationa Conference on ORGANIZED MOLECULAR FILMS (ICOMF15-LB15)

Lugar de celebración: Jeju (Corea del Sur)

Fecha: 2014

- Autores: Carlos Rubia Payá, J.J. Giner Casares, M.T. Martín Romero, D. Möbius and Luis Camacho

Título: Estudio de la Agregación y la Estructura de una tiocarbocianina en la interfase aire-agua

Tipo de participación: Comunicación Oral

Congreso: II Segunda Reunión de Jóvenes Investigadores en Coloides e Interfases (JICI II)

Lugar de celebración: Granada (España)

Fecha: 2014

- Autores: Carlos Rubia Payá, J.J. Giner Casares, M.T. Martín Romero, D. Möbius and Luis Camacho

Título: Evolution and Morphology of 2D Chiral Structures of Quinoline Derivatives at the Air-Water Interface.

Tipo de participación: Póster

Congreso: 13 European conference on organized films (ECOFF13)

Lugar de celebración: Cork (Irlanda)

Fecha: 2013

- Autores: Carlos Rubia Payá, Eugenio Jiménez Millán, Juan J. Giner Casares, Eulogia Muñoz and Luis Camacho

Título: From 2D to 3D at the Air/Water Interface: The Self-Aggregation of the Acridine Dye in Mixed Monolayers.

Tipo de participación: Póster

Congreso: 5º Iberian Meeting on colloid and interfaces (RICI5)

Lugar de celebración: San Sebastián (España)

Fecha: 2013

- Autores: Carlos Rubia Payá, Eugenio Jiménez Millán, Juan J. Giner Casares, Eulogia Muñoz and Luis Camacho

Título: Domios Hexagonales Formados por una Tricapa de la Mezcla Acridina-Ácido Esteárico en la Interfase Aire Agua

Tipo de participación: Comunicación Oral

Congreso: III Congreso Científico de Investigadores en Formación de la Universidad de Córdoba

Lugar de celebración: Córdoba (España)

Fecha: 2013

- Autores: Carlos Rubia Payá, Eugenio Jiménez Millán, Juan J. Giner Casares, Eulogia Muñoz and Luis Camacho

Título: Domios Hexagonales Formados por una Tricapa de la Mezcla Acridina-Ácido Esteárico en la Interfase Aire Agua

Tipo de participación: Póster

Congreso: IV. Encuentro sobre nanociencia y nanotecnología de investigadores y tecnólogos andaluces (NanoUco IV)

Lugar de celebración: Córdoba (España)

Fecha: 2013

- Autores: Gonzalez-Delgado, AM; **Rubia-Paya, C**; Giner-Casares, JJ; Perez-Morales, M; Munoz, E; Martin-Romero, MT; Camacho, L; Brezesinski, G

Título: Control of The Lateral Organization and Effect of the Reduction of the Available Surface Area on Langmuir Monolayers Formed by Hemicyanine

Tipo de participación: Póster

Congreso: 12th European Conference on Organized Films (ECOF12)

Lugar de celebración: Sheffield (England)

Fecha: 2011

- Autores: Gonzalez-Delgado, AM; **Rubia-Paya, C**; Jiménez Millán, E; Giner-Casares, JJ; Munoz, E; Camacho, L

Título: Organización Lateral de Monocapas Mixtas

Tipo de participación: Póster

Congreso: Encuentro sobre nanociencia y nanotecnología de investigadores y tecnólogos andaluces (NanoUco III)

Lugar de celebración: Córdoba (España)

Fecha: 2011