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Sistemas Luminiscentes Ciclometalados de Pt e Ir con Cromóforos 2-Arilbenzotiazol: Aplicaciones Biológicas y Fotocatalíticas
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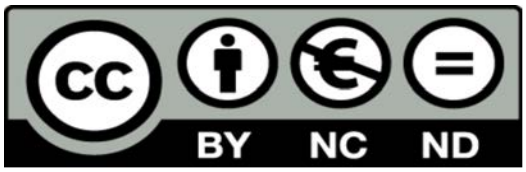

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Programa de Doctorado en Química

SISTEMAS LUMINISCENTES CICLOMETALADOS DE Pt E Ir CON CROMÓFOROS 2-ARILBENZOTIAZOL: APLICACIONES BIOLÓGICAS Y FOTOCATALÍTICAS

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CERTIFICAN:

Que la presente memoria titulada **Sistemas Luminiscentes Ciclometalados de Pt e Ir con Cromóforos 2-Arilbenzotiazol: Aplicaciones Biológicas y Fotocatalíticas** ha sido realizada en el Departamento de Química – Instituto de Investigación en Química de la Universidad de La Rioja (IQUR) bajo nuestra dirección por el graduado en Química David Gómez de Segura Zorzano y autorizan a su presentación para que sea calificado como Tesis Doctoral.

Logroño, 28 de Agosto de 2024

Fdo.: Prof. Dra. Mª Teresa Moreno García

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Abreviaciones y Siglas

Abbreviations and Acronyms

acac	Acetilacetonato	*Acetylacetonate*
ACQ	Desactivación Causada por Agregación	*Aggregation Caused Quenching*
ADC	Diamenocarbeno Acíclico	*Acycli Diaminocarbene*
ADN	Ácido Desoxirribonucleico	*Desoxyribonucleic Acid*
AIE	Emisión Inducida por Agregación	*Aggregation Induced Emission*
ATRA	Adición de Radicales por Transferencia de Átomos	*Atom Transfer Radical Addition*
B3LYP	Becke, 3-parameter, Lee-Yang-Parr	
BODIPY	4,4-difluoro-4-bora-3a,4a-diaza-s-indaceno	*4,4-difluoro-4-bora-3a,4a-diaza-s-indacene*
bpy	Bipiridina	*Bipyridine*
br	Ancho	*Broad*
bzq	7,8-benzoquinolina	*7,8-benzoquinoline*
CAM-B3LYP	Método de Atenuación Coulómbica-Becke, 3-parameter, Lee-Yang-Parr	*Coulombic Attenuation Method-Becke, 3-parameter, Lee-Yang-Parr*
C≡CR$^-$	Alquinilo	*Alkynyl*
CN$^-$	Cianuro	*Cyanide*
CNR	Isocianuro	*Isocyanide*
COSY	Espectroscopía de Correlación	*Correlation Spectroscopy*
d	Doblete	*Doublet*
D3(BJ)	Corrección de Dispersión Grimme's D3BJ	*Grimme's D3BJ Dispersion Correction*
DET	Transferencia Energética de Dexter	*Dexter Energy Transfer*
dfppy	2,4-difluorofenilpiridina	*2,4-difluorophenylpyridine*

DFT	Teoría del Funcional de la Densidad	*Density Functional Theory*
DMF	Dimetilformamida	*Dimethylformamide*
DMSO	Dimetilsulfóxido	*Dimethylsulfoxide*
δ	Desplazamiento Químico en RMN	*NMR Chemical Shift*
ECP	Potencial de Core Efectivo	*Effective Core Potential*
ESI	Ionización por Electrospray	*Electrospray Ionization*
ε	Coeficiente de Extinción Molar	*Molar Extintion Coefficient*
f	Fuerza de Oscilador	*Oscillator Strength*
f_A	Número de Fotones Absorbidos	*Number of Absorbed Photons*
f_E	Número de Fotones Emitidos	*Number of Emitted Photons*
FBS	Suero Fetal Bovino	*Fetal Bovine Serum*
FDA	Administración de Alimentos y Medicamentos de Estados Unidos	*Food and Drug Administration*
FLIM	Microscopía de Imagen por Tiempo de Vida de Fluorescencia	*Fluorescence Lifetime Imaging Microscopy*
FRET	Transferencia de Energía Resonante de Föster	*Föster Resonance Energy Transfer*
ϕ	Rendimiento Cuántico	*Quantum Yield*
GHS	Glutatión	*Glutation*
HMBC	Correlación Heteronuclear a Enlaces Múltiples	*Heteronuclear Multiple Bond Correlation*
HOMO	Orbital Molecular Ocupado Más Alto en Energía	*Highest Energy Occupied Molecular Orbital*
HS	Superficie de Hirshfeld	*Hirshfeld Surface*
HSQC	Correlación Heteronuclear a un Enlace	*Heteronuclear Single Quantum Correlation*
IC	Conversión Interna	*Internal Conversion*
i.e. / ej.	Por ejemplo	*In Expample*
IL	Intraligando	*Intraligand*
ILCT	Transferencia de Carga Intraligando	*Intraligand Charge Transfer*

ABREVIATURAS Y SIGLAS

^{i}Pr	Isopropilo	*Isopropyl*
IR	Infrarrojo	*Infrarred*
ISC	Cruce Intersistema	*Intersystem Crossing*
k_{nr}	Constante No radiativa	*Non-radiative Rate Constant*
k_r	Constante Radiativa	*Radiative Rate Constant*
λ_{abs}	Longitud de Onda de Absorción	*Absorption Wavelength*
LC	Centrada en el Ligando	*Ligand Centered*
LEC	Celda Electroquímica Emisora de Luz	*Light-Emitting Electrochemical Cell*
λ	Longitud de Onda	*Wavelength*
λ_{em}	Longitud de Onda de Emisión	*Emission Wavelength*
λ_{exc}	Longitud de Onda de Excitatión	*Excitation Wavelength*
LL'CT	Transferencia de Carga de un Ligando a otro Ligando	*Ligand to Ligand Charge Transfer*
LMCT	Transferencia de Carga del Ligando al Metal	*Ligando to Metal Charge Transfer*
LUMO	Orbital Molecular Vacío Más Bajo en Energía	*Lowest Energy Unoccupied Molecular Orbital*
m	Medio	*Medium*
m	Multiplete	*Multiplet*
m-	Meta	*Meta*
MALDI	Desorción/Ionización Láser Asistida por Matriz	*Matrix-Assisted Laser Desorption Ionization*
max	Máximo	*Maximum*
MC	Centrado en el Metal	*Metal-Centered*
Me	Metil	*Methyl*
MLCT	Transferencia de Carga del Metal al Ligando	*Metal to Ligand Charge Transfer*
MMCT	Transferencia de Carga Metal-Metal	*Metal-Metal Charge Transfer*
MMLCT	Transferencia de Carga Metal-Metal al Ligando	*Metal-Metal-to-Ligand Charge Transfer*

6-MP	6-Mercaptopurina	*6-Marcaptopurine*
NCI	Interacciones No Covalentes	*Non-Covalent Interactions*
NER	Mecanismo de reparación del ADN por Escisión de Nucleótidos	*Nucleotide Excision Repair*
NHC	N-Carbenos Heterocíclicos	*N-Heterocyclic Carbene*
NIR	Infrarrojo Cercano	*Near Infrarred*
nm	Nanómetro	*Nanometer*
RMN/NMR	Resonancia Magnética Nuclear	*Nuclear Magnetic Resonance*
o-	Orto	*Ortho*
OLED	Diodo Orgánico Emisor de Luz	*Organic Light-Emitting Diode*
p-	Para	*Para*
pbt	2-fenilbenzotiazol	*2-phenylbenzothiazole*
PC	Fotocatalizador	*Photocatalyst*
PCM	Modelo del Continuo Polarizable	*Polarizable Continuum Model*
PDT	Terapia Fotodinámica	*Photodynamic Therapy*
phen	1,10-Fenantrolina	*1,10-Phenanthroline*
piq	1-fenilisoquinolina	*1-phenylisoquinoline*
PLIM	Microscopía de Imagen por Tiempo de Vida de Fosforescencia	*Phosphorescence Lifetime Imaging Microscopy*
ppy	2-fenilpiridina	*2-phenylpyridine*
PS	Poliestireno / Fotosensitizador	*Polystyrene / Photosensitizer*
PTA	1,3,5-triaza-7-fosfaadamantano	1,3,5-triaza-7-phosphaadamantane
PXRD	Difracción de Rayos X de Polvo	*Powder X-Ray Diffraction*
py	Piridina	*Pyridine*
RDG	Gradiente de Densidad Reducida	*Reduced Density Gradient*
RISC	Cruce Intersistema Inverso	*Reverse Intersystem Crossing*
ROS	Especies Reactivas de Oxígeno	*Reactive Oxygen Species*
RT	Temperatura Ambiente	*Room Temperature*
s	Singlete	*Singlet*
s	Fuerte	*Strong*
S_0	Estado Fundamental	*Ground State*

ABREVIATURAS Y SIGLAS

SCF	Autoconsistencia de Campo	*Self Consistent Field*
SET	Transferencia Monoelectrónica	*Single Electron Transfer*
sh	Hombro	*Shoulder*
S_n	Estado Singlete Excitado	*Excited Singlet State*
SOMO	Orbital Molecular Ocupado por un Electrón	*Single Occupied Molecular Orbital*
τ	Tiempo de Vida de Emisión	*Emission Lifetime*
t	Triplete	*Triplet*
TADF	Fluorescencia Retardada Activada Térmicamente	*Thermally Activated Delayed Fluorescence*
TD-DFT	Teoría del Funcional de la Densidad Dependiente del Tiempo	*Time Dependent-Density Functional Theory*
TEM	Microscopía Electrónica de Transmisión	*Transmission Electron Microscopy*
THF	Tetrahidrofurano	*Tetrahydrofuran*
thpy	2-(2-tienil)piridina	*2-(2-thienyl)pyridine*
T_n	Estado Excitado Triplete	*Triplet Excited State*
TOCSY	Espectroscopía de Correlación Total	*Total Correlation Spectroscopy*
TOF	Tiempo de Vuelo	*Time of Flight*
TPPTS	Sal Trisódica de ácido trifenilfosfina-3,3',3''- trisulfónico	*3,3',3''-phosphatryiltris(benzenosulfonic acid) trisodium salt*
TTA	Aniquilación Triplete-Triplete	*Triplet-Triplet Annihilation*
TzR	Tetrazolato	*Tetrazolate*
UP	Conversión Ascendente	*Upconversion*
UV-Vis	Ultravioleta-Visible	*Ultraviolet-Visible*
VOC	Compuestos Orgánicos Volátiles	*Volatile Organic Compounds*
VR	Relajación Vibracional	*Vibrational Relaxation*
vs	Muy Fuerte	*Very Strong*
w	Débil	*Weak*

WOLED	Diodo Orgánico Emisor de Luz Blanca	*White Organic Light-Emitting Diode*

Resumen
Summary

Resumen

Los complejos de coordinación de metales de transición con ligandos aromáticos conjugados han constituido un área de interés en las últimas décadas debido a su amplia variedad de aplicaciones asociadas a sus interesantes propiedades optoelectrónicas y a la gran versatilidad de modulación en función del entorno y la naturaleza de los coligandos. En este contexto, esta Tesis Doctoral, se centra en la síntesis, caracterización, estudio de propiedades y posibles aplicaciones biológicas y fotocatalíticas de nuevos sistemas luminiscentes basados en complejos ciclometalados con la unidad 2-arilbenzotiazol de Pt e Ir con diferentes coligandos.

Se ha preparado una serie de complejos ciclometalados de Pt^{II} con el ligando 2-fenilbenzotiazol (pbt) de tipo [Pt(pbt)(PPh_2(R)-κ*P,O*)] con coligandos quelato voluminosos derivados de difenilfosfinas funcionalizadas con ácidos deprotonados, cuyas propiedades ópticas y estructurales se compararon con los análogos de Ir^{III} de fórmula [$Ir(pbt)_2$(PPh_2(R)-κ*P,O*)]. El análisis de las propiedades fotoluminiscentes y los cálculos teóricos TD-DFT sugieren que los ligandos P^O ejercen escasa o nula influencia en los estados excitados. Los compuestos de Pt^{II} muestran mayor contribución metálica en las transiciones electrónicas involucradas en las propiedades ópticas y rendimientos cuánticos superiores, en comparación con los de Ir^{III}. Además, se han preparado dos familias de compuestos de Pt^{II} con los ligandos ciclometalados pbt y 2-(4-dimetilaminofenil)benzotiazol (Me_2N-pbt) con coligandos picolinato de tipo [Pt(R-pbt)(R'-pic-κ*N,O*)] (R = H, Me_2N; R'= H, OH), de geometría plana que permite establecer interacciones Pt···Pt y/o π···π. En éstos, la variación del sustituyente en el ligando quelato picolinato y el disolvente de cristalización genera diferentes tipos de fases con empaquetamientos y propiedades ópticas diferentes, además de presentar propiedades mecanocrómicas. Además, los derivados con la funcionalización Me_2N-pbt muestran emisiones duales, generación de oxígeno singlete y capacidad antiproliferativa, que se ha estudiado, en condiciones de oscuridad y fotoinducción frente a líneas tumorales de cáncer de pecho y de

pulmón (MDA-MB-231 y A549) y no tumoral de pecho (MCF10A), en colaboración con el Instituto de Química Molecular de la Universidad de La Sorbona.

Por otro lado, se ha descrito una serie de compuestos mononucleares con ligandos pirazol de tipo $[Pt(pbt)(R'_2\text{-}pzH)_2]PF_6$ y binucleares (Pt^{II}-Pt^{II}) $[Pt(pbt)(\mu\text{-}R'_2pz)]_2$ y $[Pt(Me_2N\text{-}pbt)(\mu\text{-}pz)]_2$ con ligandos pirazolato puente. Los compuestos de Pt^{II} $[Pt(R\text{-}pbt)(\mu\text{-}pz)]_2$ muestran una elevada tendencia a oxidarse en $CHCl_3$ y en presencia de luz solar dando lugar a derivados de bimetálicos, Pt^{III}-Pt^{III}, $[Pt(R\text{-}pbt)(\mu\text{-}pz)Cl]_2$ con la formación de enlace Pt-Pt. El derivado binuclear de Pt^{II} con el sustituyente dimetilamino en la unidad ciclometalada muestra una emisión dual, Fluorescencia y Fosforescencia, dependiente de la longitud de onda de excitación. Este compuesto muestra capacidad de generación de $^1O_2$, que ha sido analizada con detalle y evaluada en la foto-oxidación de *p*-bromotioanisol $[Me(BrC_6H_4)S]$ a metil-bromofenilsulfóxido $[Me(BrC_6H_4)SO]$ con luz azul.

Finalmente, se describe la síntesis de una serie de derivados heterolépticos pentafluorofenil-bis(2-fenilbenzotiazol) de Pt^{IV} de tipo $[Pt(pbt)_2(C_6F_5)L]^{n+}$ (n = 0, 1) (L= N-dadores y $OCOCF_3$) y el complejo binuclear $[\{Pt(pbt)_2(C_6F_5)\}_2(\mu\text{-bpyb})](PF_6)_2$. La variación en el ligando en posición *trans* al carbono metalado nos ha permitido examinar su influencia en las propiedades ópticas (absorción y emisión) y en su lipofilia, esta última estrechamente relacionada con la permeabilidad y metabolismo de las moléculas en las células. Se ha evaluado también, en colaboración con el CIBIR, la actividad citotóxica y la interacción con el ADN de algunos derivados seleccionados.

Summary

Coordination transition metal complexes with conjugated aromatic ligands have been an area of interest in recent years due to their wide variety of applications associated with their interesting optoelectronic properties and the great versatility of modulation depending on the environment and the nature of the coligands. In this context, this PhD Thesis focuses on the synthesis, characterization, study of the properties and possible biological and photocatalytic applications of new luminescent systems based on cyclometalated Pt and Ir complexes with the 2-arylbenzothiazole unit with different coligands.

A series of cyclometalated Pt^{II} complexes, [Pt(pbt)(PPh_2(R)-$\kappa P,O$)], with 2-phenylbenzothiazole (pbt) as chromophore and featuring chelating deprotonated diphenylphosphines functionalized (acid groups) as coligands, have been prepared and their optical and electronic properties have also been compared with those of related Ir^{III} derivatives, [$Ir(pbt)_2$(PPh_2(R)-$\kappa P,O$)]. Analysis of photoluminescent properties and theoretical TD-DFT calculations suggest that P^O ligands exert scarce or no influence on the excited states. Pt^{II} compounds show greater metallic contribution in the electronic transitions involved in optical properties and higher quantum yields, compared to those of Ir^{III}. In addition, two families of Pt^{II} compounds with picolinate as coligands of type [Pt(R-pbt)(R'-pic-$\kappa N,O$)] (R = H, NMe_2; R' = H, OH), exhibiting Pt···Pt and/or $\pi\cdots\pi$ interactions, have been prepared. In these complexes, the variation of the substituent in the picolinate chelate ligand and the crystallization solvent originate different types of solid phases with distinct optical properties and also mechanochromic behavior. Furthermore, the Me_2N-pbt complexes show dual emissions, singlet oxygen generation and antiproliferative ability. This latter has been studied against breast and lung cancer tumour cell lines (MDA-MB-231 and A549) and non-tumour breast cell line (MCF10A), in collaboration with the Institute of Molecular Chemistry of the Sorbonne University, in the dark and under photoinduction conditions.

On the other hand, a series of mononuclear compounds with pyrazole ligands, $[Pt(pbt)(R'_2\text{-}pzH)_2]PF_6$ and binuclear (Pt^{II}-Pt^{II}) derivatives with bridging pyrazolate ligands, $[Pt(pbt)(\mu\text{-}R'_2pz)]_2$ and $[Pt(Me_2N\text{-}pbt)(\mu\text{-}pz)]_2$, have been synthetized. The bimetallic compounds, $[Pt(R\text{-}pbt)(\mu\text{-}pz)]_2$, show a high tendency to oxidize in $CHCl_3$ and in the presence of sunlight, giving rise to binuclear derivatives of Pt^{III}-Pt^{III} $[Pt(R\text{-}pbt)(\mu\text{-}pz)Cl]_2$ with a covalent Pt-Pt bond. The Pt^{II}-Pt^{II} binuclear derivative of Pt^{II} featuring the Me_2N-pbt cyclometalated unit shows a dual emission, Fluorescence and Phosphorescence, depending on the excitation wavelength. In addition, this compound shows $^1O_2$ generation capacity, which has been analyzed in detail and evaluated in the photooxidation process of *p*-bromothioanisole to methyl-*p*-bromophenylsulfoxide $[Me(BrC_6H_4)SO]$ with blue light.

Finally, the synthesis of a series of heteroleptic pentafluorophenyl-bis(2-phenylbenzothiazole) derivatives of Pt^{IV} of type $[Pt(pbt)_2(C_6F_5)L]^{n+}$ (n = 0, 1) (L= N-donor and $OCOCF_3$) and of the binuclear complex $[\{Pt(pbt)_2(C_6F_5)\}_2(\mu\text{-bpyb})](PF_6)_2$ has been carried out. The variation of the ligand located in the *trans* position to the metalated carbon has allowed us to study its influence on the optical properties (absorption and emission) and lipophilicity, this latter closely related to the permeability and metabolism of the molecules in cells. The cytotoxic activity and interaction with DNA of some selected derivatives has also been evaluated, in collaboration with the CIBIR.

Presentación

Presentación

En esta Tesis, titulada “Sistemas luminiscentes ciclometalados de Pt e Ir con cromóforos 2-arilbenzotiazol: aplicaciones biológicas y fotocatalíticas”, se presenta como un conjunto de artículos científicos publicados a lo largo del período de investigación, que tratan sobre síntesis, estudio de propiedades ópticas, biológicas y fotocatalíticas de diferentes familias de compuestos ciclometalados de Pt e Ir basados en la unidad 2-arilbenzotiazol. La parte II del Capítulo 3 no ha sido publicada, pero se presenta en formato de artículo científico, puesto que se enviará próximamente para su publicación.

Esta Memoria de Tesis Doctoral comienza con una primera sección introductoria en la que se plantean los conocimientos teóricos acerca de la temática de la Tesis. En la primera parte se describen los conceptos de luminiscencia y concretamente la luminiscencia en complejos de Pt^{II}, Pt^{IV} e Ir^{III}, haciendo hincapié en las interesantes propiedades de agregación que tienen los complejos plano-cuadrados de Pt^{II}, lo que les confiere una amplia variedad de estados excitados muy sensibles a diferentes estímulos externos, como solvatocromismo, vapocromismo, termocromismo, mecanocromismo o una combinación de estos, exhibiendo propiedades multifuncionales.

A continuación, se presentan conceptos básicos sobre la aplicación de la Química Computacional y los Cálculos Teóricos a los sistemas presentados en la Memoria.

En la siguiente sección de esta parte introductoria, se detallan de forma breve las propiedades biológicas de los complejos de Pt, focalizando el interés en los compuestos ciclometalados de Pt^{II} como agentes antitumorales y de bioimagen y en los derivados de Pt^{IV} como profármacos multiplataforma. Finalmente, en esta misma sección, se presentan los diferentes mecanismos de la Terapia Fotodinámica.

En el siguiente apartado se introducen los diferentes tipos de fotocatálisis y las características y antecedentes de compuestos metálicos de Ru^{II}, Ir^{III} y Pt^{II} empleados como fotocatalizadores.

La introducción finaliza con una sección sobre los antecedentes de compuestos ciclometalados de Pt^{II}, Pt^{IV} e Ir^{III} con ligandos derivados del fenilbenzotiazol. Seguidamente, se detallan los objetivos planteados en el presente trabajo de investigación.

Posteriormente, esta Memoria de Tesis Doctoral se divide en cuatro capítulos dedicados a diferentes artículos científicos en el idioma original de publicación (inglés). La Información Suplementaria se incluye al final de cada uno de los capítulos. A continuación, se ofrece un breve resumen del contenido de cada capítulo:

Capítulo 1:

En este trabajo se presenta la síntesis y caracterización de dos series de compuestos ciclometalados de Pt^{II} e Ir^{III} de tipo [Pt(pbt){PPh_2(R)-κ*P,O*}] (**2a**-**2c**) y [Ir(pbt)$_2$({PPh_2(R)-κ*P,O*}] (**3a-3c**), donde pbt es 2-fenilbenzotiazol y PPh_2(R) son difenilfosfinas funcionalizadas con ácidos deprotonados (R = *o*-$C_6H_4CO_2$ **a**, *o*-$C_6H_4SO_3$ **b**, $CH_2CH_2CO_2$ **c**). Las estructuras de los compuestos **1**, **2a-2c**, **3a** y **3b** se han confirmado por difracción de Rayos X de monocristal. Se ha realizado un estudio de Superficies de Hirshfeld y de Interacciones No Covalentes (NCI) de la estructura supramolecular del complejo **2a**. Se han estudiado con detalle las propiedades fotofísicas de absorción y emisión (en diferentes medios) de todos los compuestos con el apoyo de cálculos teóricos y se han extraído conclusiones que permiten comparar los sistemas de Pt^{II} e Ir^{III}. Los compuestos de Pt^{II} exhiben una intensa luminiscencia en la región de 525 – 543 nm, que se asigna a transiciones de tipo ^{3}IL, con menor contribución ^{3}MLCT (L = pbt). Los complejos de Ir^{III} muestran emisiones naranjas (534 – 584 nm a temperatura ambiente), que se desplazan hipsocrómicamente al bajar la temperatura (527–560 nm a 77 K), de carácter mixto ^{3}IL/^{3}MLCT/^{3}LLCT. Además, los compuestos de Pt (**2a-2c**) muestran rendimientos

cuánticos en films de poliestireno superiores a los de Ir^{III} y el complejo precursor solvato de DMSO **1**. La diferencia energética calculada entre los estados ^{3}MC-^{3}IL/^{3}MLCT para los complejos **2a** y **3a** se correlaciona con el mayor rendimiento cuántico encontrado para los complejos de Pt en relación con los de Ir.

Capítulo 2:

Este capítulo se divide en dos partes referidas a la coordinación de ligandos quelato de tipo picolinato:

- Una primera parte en la que se presentan dos nuevos compuestos ciclometalados de Pt^{II} con el ligando 2-fenilbenzotiazol (pbt) y dos ligandos quelato picolinato diferentes [Pt(pbt)(R-pic-κ*N,O*)] (R = H (**1**), OH (**2**)). A diferencia de **1**, la introducción del sustituyente hidroxilo en el compuesto **2**, permite obtener diferentes empaquetamientos debido a la posibilidad de establecer interacciones de enlace de hidrógeno de tipo dador-aceptor con moléculas de CH_2Cl_2 de disolvente. Así, se han conseguido aislar tres pseudopolimorfos del compuesto **2** con diferente grado de agregación: amarillo **2-Y**, naranja-rojo **2-R** (**2·0.5CH_2Cl_2**) y negro **2-B** (**2·0.75CH_2Cl_2**), con emisiones en estado sólido a temperatura ambiente de 540, 656 y 740 nm, respectivamente. Las fases **2-R** y **2-B** pueden transformarse al sólido amarillo original **2**. Los estudios de difracción de Rayos-X de monocristal para los compuestos **1** y **2-Y** muestran una estructura supramolecular en columnas con apilamientos π···π únicamente, mientras que **2-R** muestra una estructura unidimensional (1D) basada en interacciones metalofílicas Pt···Pt y π···π, en concordancia con sus colores y las propiedades fotofísicas, evaluadas en diversos medios. Adicionalmente, ambos compuestos muestran un comportamiento mecanocrómico reversible con gran contraste de color y emisión tras presionarlo, sufriendo una transición entre fases cristalinas y amorfas, confirmado por difracción de Rayos-X de polvo (PXRD). Los cálculos teóricos revelan que las interacciones Pt···Pt son más fuertes en trímeros y tetrámeros, que en los dímeros,

especialmente en los estados T_1 de carácter ^{3}IL/^{3}MLCT para el monómero y de tipo ^{3}MM(L+L')CT para los oligómeros. Estudios teóricos de Interacciones No Covalentes (NCI) indican que las interacciones π···π entre los ligandos quelatos presentan gran influyen en el carácter de transferencia de carga metal-metal-ligando de la transición.

- En la segunda parte se describe la preparación, propiedades ópticas, generación de oxígeno singlete y propiedades biológicas de compuestos ciclometalados de Pt^{II} con el ligando 2-(4-dimetilaminofenil)benzotiazol (Me_2N-pbt) y distintos ligandos de tipo picolinato [Pt(Me_2N-pbt)(R-pic-κ*N,O*)] (R = 3-H **1**, 3-NH_2 **2**, 3-OH **3**, 4-COOH **4**). Estudios de difracción de Rayos-X sobre los compuestos **1** y **3·CHCl₃** muestran cadenas infinitas 1D basadas en agregados de tipo π···π para el compuesto **1** o de tipo Pt···Pt y π···π para **3**, obteniendo estructuras basadas en cadenas infinitas (1D). Las emisiones fosforescentes de los compuestos **1**-**3** tienen un carácter ^{3}ILCT con escasa contribución metálica, mientras que el compuesto **4** muestra un carácter mixto ^{3}LL'CT/^{3}ILCT (L = Me_2N-pbt, L' = pic), en concordancia con los cálculos teóricos. Adicionalmente, en CH_2Cl_2 a temperatura ambiente todos los compuestos muestran emisiones duales con fluorescencias adicionales de carácter ^{1}(M+L)L'CT (**1**-**3**), ^{1}LL'CT/^{1}ILCT ó ^{1}(M+L)L'CT (**4**), dependiendo de la longitud de onda de excitación. En general, los compuestos **1**-**3** muestran buenos rendimientos cuánticos de generación de oxígeno singlete (ϕ_Δ $^1O_2$ 13.6-17.4%). Finalmente, se ha analizado la actividad biológica de estos compuestos frente a las líneas de cáncer de pecho celulares triple negativa (MDA-MB-231), adenocarcinoma de pulmón (A549) y la no tumoral de pecho (MCF10A) en condiciones de oscuridad y bajo irradiación de 5 minutos con luz azul (450 nm).

Capítulo 3:

En este capítulo se describe la síntesis de compuestos mononucleares con ligandos pirazol de tipo [Pt(pbt)(R'$_2$-pzH)$_2$]PF_6 (R'$_2$-pzH = pzH **1a**, 3,5-Me_2pzH **1b**, 3,5-$^i Pr_2$pzH **1c**) y binucleares con ligandos pirazolato puente (Pt^{II}-Pt^{II}), [Pt(pbt)(μ-R'$_2$pz)]$_2$

(R'_2-pz = pz **2a**, 3,5-Me_2pz **2b**, 3,5-$^i Pr_2$pz **2c**) y [Pt(Me_2N-pbt)(μ-pz)]$_2$ (**3a**). Los compuestos **2a** y **3a** evolucionan en disolución de $CHCl_3$ y luz solar a los correspondientes derivados de Pt^{III}-Pt^{III} [Pt(R-pbt)(μ-pz)Cl]$_2$ (R = H **4a**, NMe_2 **5a**). Los estudios experimentales y computacionales revelan la nula influencia de los ligandos pirazol o pirazolato en las propiedades ópticas de los compuestos **1a-c** y **2a**,**b**, que exhiben una emisión ^{3}IL/^{3}MLCT, mientras que el compuesto **2c** presenta algo de contribución ^{3}MMLCT en la emisión. El derivado **3a** muestra una emisión dual, dependiente de la longitud de onda de excitación, una Fluorescencia (^{1}ILCT o ^{1}MLCT/^{1}LC) y una Fosforescencia (^{3}ILCT). La Fosforesencia se pierde en disoluciones aireadas debido a la transferencia energética al $^3O_2$ para producir $^1O_2$. La emisión fosforescente puede fotoinducirse (365 nm, ~ 15 min) reversiblemente en disoluciones oxigenadas de THF y DMSO. Para los compuestos de Pt_2^{III} (**4a** y **5a**) las transiciones electrónicas de baja energía (S_1-S_3) tienen carácter mixto (LMMCT/LXCT/L'XCT **4a**; LMMCT/LXCT/ILCT **5a**) y son poco emisivos, únicamente en medio rígidos. Se ha evaluado la capacidad de generación de $^1O_2$ del complejo **3a** empleando este compuesto como fotocatalizador en el proceso de fotooxidación en presencia de oxígeno del *p*-bromotioanisol.

Capítulo 4:

En este último capítulo se presenta una nueva familia de compuestos luminiscentes heterolépticos pentafluorofenil-bis(2-fenilbenzotiazol) de Pt^{IV} de tipo *fac*-[Pt(pbt)$_2$(C_6F_5)L]$^{n+}$ (n = 1, 0) [L= 4-Mepy **1**, 4-piridilbenzotiazol (pybt) **2**, 4,4'-bipiridina (4,4'-bpy) **3**, 1,2-bis-(4-piridil)etileno (bpe) **4** (*E/Z* ratio 90/10), 1,4-bis-(piridil)butadiino (bpyb) **5**, trifluoroacetato ($^-$OCOCF_3) **6**] y el complejo binuclear [{Pt(pbt)$_2$(C_6F_5)}$_2$(μ-bpyb)](PF_6)$_2$ **7**, en los que se ha variado el ligando *trans* al carbono metalado del pbt para modificar las propiedades ópticas y la lipofilia. Se han estudiado las propiedades fotofísicas de forma experimental y teórica mostrando una gran dependencia del ligando N-dador coordinado al centro de Pt^{IV}. Así, los compuestos **1**, **3** y **6** presentan, en diferentes medios, emisiones debidas a estados excitados de tipo intraligando ^{3}ILCT localizados en el ligando 2-fenilbenzotiazol, mientras que las emisiones de **2**, **5** y **7** se han adscrito a una

mezcla de estados próximos en energía de tipo ^{3}IL'(N-dador)/^{3}ILCT(pbt), como confirman las medidas de tiempos de vida de emisión y los cálculos teóricos. La irradiación de la mezcla inicial *E/Z* del complejo **4** durante 15 minutos llevan a un estado fotoestacionario con una composición 1:1.15 (*E:Z*). Este complejo no es emisivo a temperatura ambiente debido a la fácil foto-isomerización *intramolecular* del ligando 1,2-bis-(4-piridil)etileno (bpe). Los complejos **1**-**3** y **6** muestran excelentes rendimientos cuánticos de generación de oxígeno singlete en disoluciones de Acetonitrilo, con valores de $\phi(^1O_2)$ entre 0.66 a 0.86 empleando la fenalenona como referencia. Los derivados catiónicos **1**-**3** exhiben altas toxicidades en concentraciones nanomolares en las líneas celulares A549 (cáncer de pulmón) y HeLa (Cáncer de Cérvix) con una buena selectividad frente a las células no tumorales BEAS-2B (epitelio pulmonar). El compuesto **6** muestra una menor toxicidad hacia la línea tumoral A549 (IC_{50}: 29.40 μM) y una elevada fotocitotoxicidad (IC_{50}: 5.75) cuando las células se irradian con luz azul durante 15 minutos. Estos compuestos no muestran evidencias de interacción con el ADN.

Lista de Artículos

Los artículos de investigación publicados incluidos en esta Tesis Doctoral son:

Capítulo 1:

David Gómez de Segura, Rebeca Lara, Mónica Martínez-Junquera, Elena Lalinde and M. Teresa Moreno. Luminescent 2-Phenylbenzothiazol Cyclometalated Pt^{II} and Ir^{III} Complexes with Chelating P^O Ligands. *Dalton Transactions*, **2022**, *51*, 274–285. https://doi.org/10.1039/D1DT03531B

Índice de Impacto: 4.0; Q1; 7/42; Área Temática: Chemistry, Inorganic and Nuclear-SCI; JCR 2022

Capítulo 2:

David Gómez de Segura, Elena Lalinde and M. Teresa Moreno. Polymorphism and Mechanochromism in 2-Phenylbenzothiazole Cyclometalated Pt^{II} Complexes with Chelating N^O Ligands. *Inorganic Chemistry*, **2022**, *61*, 20043–20056. https://doi.org/10.1021/acs.inorgchem.2c03423

Índice de Impacto: 4.6; Q1; 5/42; Área Temática: Chemistry, Inorganic and Nuclear-SCI; JCR 2022

Capítulo 3:

David Gómez de Segura, Andrea Corral-Zorzano, Eduardo Alcolea, M. Teresa Moreno and Elena Lalinde. Phenylbenzothiazole-based Platinum(II) and Diplatinum(II) and (III) Complexes with Pyrazolate Groups: Optical Properties and Photocatalysis. *Inorganic Chemistry*, **2024**, *63*, 1589–1606. https://doi.org/10.1021/acs.inorgchem.3c03532

Índice de Impacto: 4.3; Q1; 8/44; Área Temática: Chemistry, Inorganic and Nuclear-SCI; JCR 2023

Capítulo 4:

David Gómez de Segura, Nora Giménez, David Rincón-Montón, M. Teresa Moreno, José G. Pichel, Íciar P. López and Elena Lalinde. A New Family of Luminescent $[Pt(pbt)_2(C_6F_5)L]^{n+}$ (n = 1, 0) Complexes: Synthesis, Optical and Cytotoxic Studies. *Dalton Transactions*, **2023**, *53*, 12390–12403. https://doi.org/10.1039/D3DT01759A

Índice de Impacto: 3.5; Q2; 13/44; Área Temática: Chemistry, Inorganic and Nuclear-SCI; JCR 2023

Conclusiones Generales

Conclusiones Generales

Las conclusiones de cada uno de los trabajos incluidos en esta Tesis se exponen al final de cada capítulo. A continuación, se resaltan las conclusiones generales:

- Se han sintetizado compuestos ciclometalados de Pt^{II} e Ir^{III} basados en la unidad 2-fenilbenzotiazol (pbt) y ligandos P^O quelato, con un fragmento PPh_2 π-aceptor funcionalizado con una unidad ácida deprotonada del tipo [Pt(pbt)(PPh_2(R)-κ*P,O*)] y [$Ir(pbt)_2$(PPh_2(R)-κ*P,O*)]. Se ha puesto de manifiesto que el ligando quelato P^O no influye en las propiedades fotoluminiscentes, pero sí el centro metálico. En los compuestos de Pt^{II} la fosforescencia es de carácter principalmente ^{3}IL con cierta contribución ^{3}MLCT, mientras que en los de Ir^{III} se origina de estados excitados mixtos ^{3}IL/^{3}MLCT/^{3}LLCT. Los compuestos de Pt^{II} mostraron rendimientos cuánticos en films de poliestireno mayores que los análogos de Ir^{III}, hecho que se correlaciona con la mayor diferencia energética calculada entre los estados electrónicos ^{3}MC-^{3}IL/^{3}MLCT para los compuestos de Pt^{II} en relación a los de Ir^{III}.
- Por otro lado se han presentado dos series de complejos ciclometalados de Pt^{II} con ligandos pbt y 2-(4-dimetilaminofenil)benzotiazol (Me_2N-pbt) y coligandos picolinato funcionalizados.
    - Se ha realizado un estudio combinado estructural, fotofísico y computacional de dos compuestos de Pt^{II}-pbt con ligandos quelato de tipo picolinato. A pesar de que solo se diferencian en un sustituyente OH, las diferencias topológicas son muy importantes. Así, el compuesto [Pt(pbt)(OH-pic-κ*N,O*)] presenta diferentes pseudopolimorfos en función del grado de agregación de las moléculas (Amarillo, Rojo y Negro) con emisiones desde el amarillo hasta en infrarrojo cercano, debido a la formación de interacciones de tipo dador-aceptor de enlaces de hidrógeno entre la función hidroxilo del ligando picolinato y moléculas de CH_2Cl_2 de cristalización. Ambos compuestos muestran mecanocromismo luminiscente reversible,

exhibiendo un desplazamiento en la emisión y absorción hacia el rojo y una transformación de fase cristalina-amorfa tras ser presionados. Los estudios teóricos sobre sistemas agregados mostraron mayor fortaleza de las interacciones metalofílicas Pt···Pt en trímeros y tetrámeros en relación a los dímeros.

- Por otra parte, el estudio de los compuestos con el sustituyente dador-aceptor dimetilamino en el fragmento ciclometalado revela que los compuestos con los sustituyentes R-pic = 3-H, 3-NH_2 y 3-OH muestran propiedades ópticas similares que difieren del compuesto con el ácido (4-COOH). Aunque todos presentan emisiones duales Fosforescencias(P)/Fluorescencia(F), en los primeros se asignan a (P)^{3}ILCT/(F)^1(M+L)L'CT, mientras que el del ácido a (P)^{3}LL'CT/^{3}ILCT/(F)^{1}LL'CT/^{1}ILCT ó ^{1}(M+L)L'CT dependiente de la λ_{exc}. Todos los compuestos muestran rendimientos cuánticos de generación de $^1O_2$ moderados (13.6-17.4%). Los resultados de la actividad antiproliferativa de los primeros revelan una elevada citotoxicidad para todos los compuestos en todas las líneas celulares ensayadas, a diferencia de las encontradas para el compuesto con la funcionalización ácido. Además, la actividad antineoplásica bajo irradiación de 5 minutos con luz azul de 450 nm, aporta resultados de índice de fotoinducción muy elevados para el compuesto con el sustituyente hidroxilo en la línea celular MDA-MB-231.

- Se prepararon nuevos compuestos cicloplatinados monometálicos y bimetálicos de Pt^{II} y Pt^{III} con ligandos pirazol y pirazolato puente de tipo *butterfly* incorporando los ligandos pbt y Me_2N-pbt como ligandos ciclometalados. Los compuestos exhiben transiciones electrónicas desde estados de tipo mayoritariamente IL/MLCT. La introducción del grupo dimetilamino favorece que los compuestos muestren emisiones duales, una fluoresencia (^{1}ILCT o ^{1}MLCT/^{1}IL) y fosforescencia (^{3}ILCT), que puede ser reversiblemente fotoinducida en disoluciones oxigenadas (DMSO y THF), bajo continua irradiación con luz ultravioleta (365 nm) causado por una

sensibilización local atribuída a transferencia energética al oxígeno molecular del medio para producir $^1O_2$. La sensibilización de oxígeno singlete fue utilizada en la fotooxidación del *p*-bromotioanisol con luz azul (460 nm), observando la contribución al mecanismo tanto del $^1O_2$ como de radicales superóxidos. Finalmente, los complejos bimetálicos Pt^{III}-Pt^{III} mostraron emisiones muy débiles en medios rígidos atribuidas a estados localizados en el ligando ciclometalado R-pbt ^{3}ILCT.

- La sustitución de ligando Cl^- de la esfera de coordinación del complejo precursor de Pt^{IV} *fac*-[Pt(pbt)$_2$(C_6F_5)Cl] con ligandos monodentados N-dadores ó CO_2CF_3 ha dado lugar a los compuestos *fac*-[Pt(pbt)$_2$(C_6F_5)L]$^{n+}$ (n = 0 , 1) y al compuesto binuclear [{Pt(pbt)$_2$(C_6F_5)}$_2$(μ-bpyb)]$^{2+}$. Los estudios experimentales y teóricos de las propiedades optoelectrónicas muestran una elevada dependencia del ligando L coordinado al centro metálico en las propiedades optoelectrónicas. Algunos derivados muestran excelente capacidad de generación de $^1O_2$ con elevados ϕ($^1O_2$). Los derivados catiónicos presentan una elevada citotoxicidad, en el rango nanomolar, para las líneas tumorales A549 y HeLa, y buena selectividad frente a las no tumorales BEAS-2B. El derivado *fac*-[Pt(pbt)$_2$(C_6F_5)($OCOCF_3$)] presenta una elevada fotocitotoxicidad cuando se irradia con luz azul, mientras que no es citotóxico en la oscuridad. No se encontraron evidencias de interacción de estos derivados con el ADN.

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