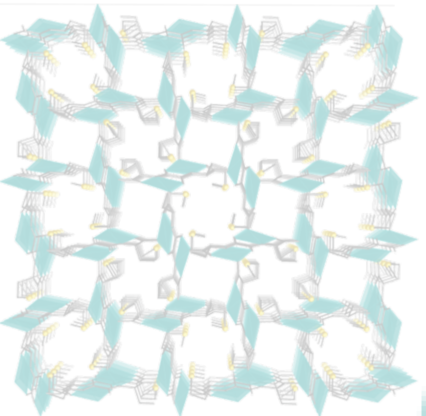
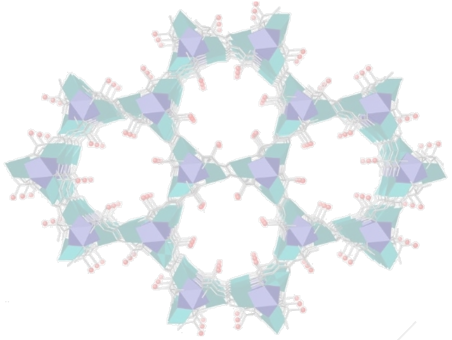
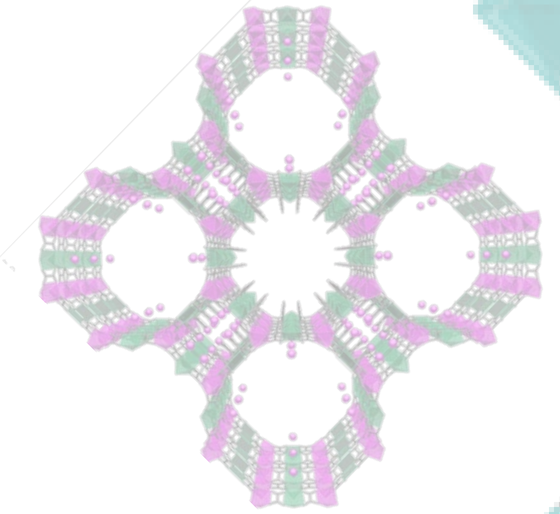
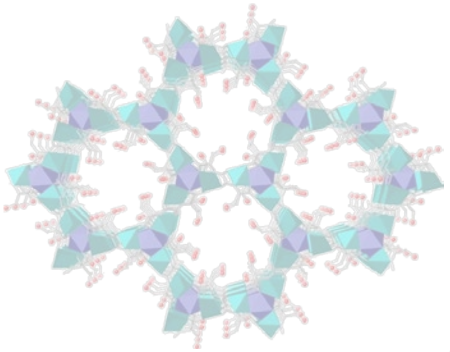
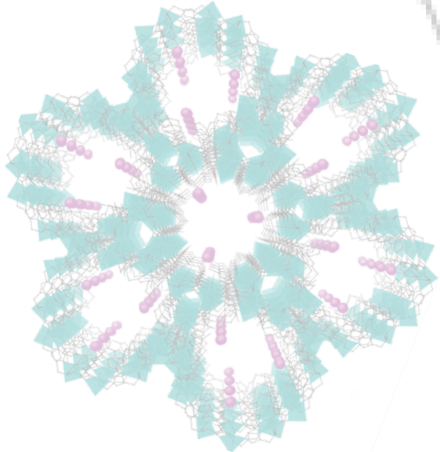






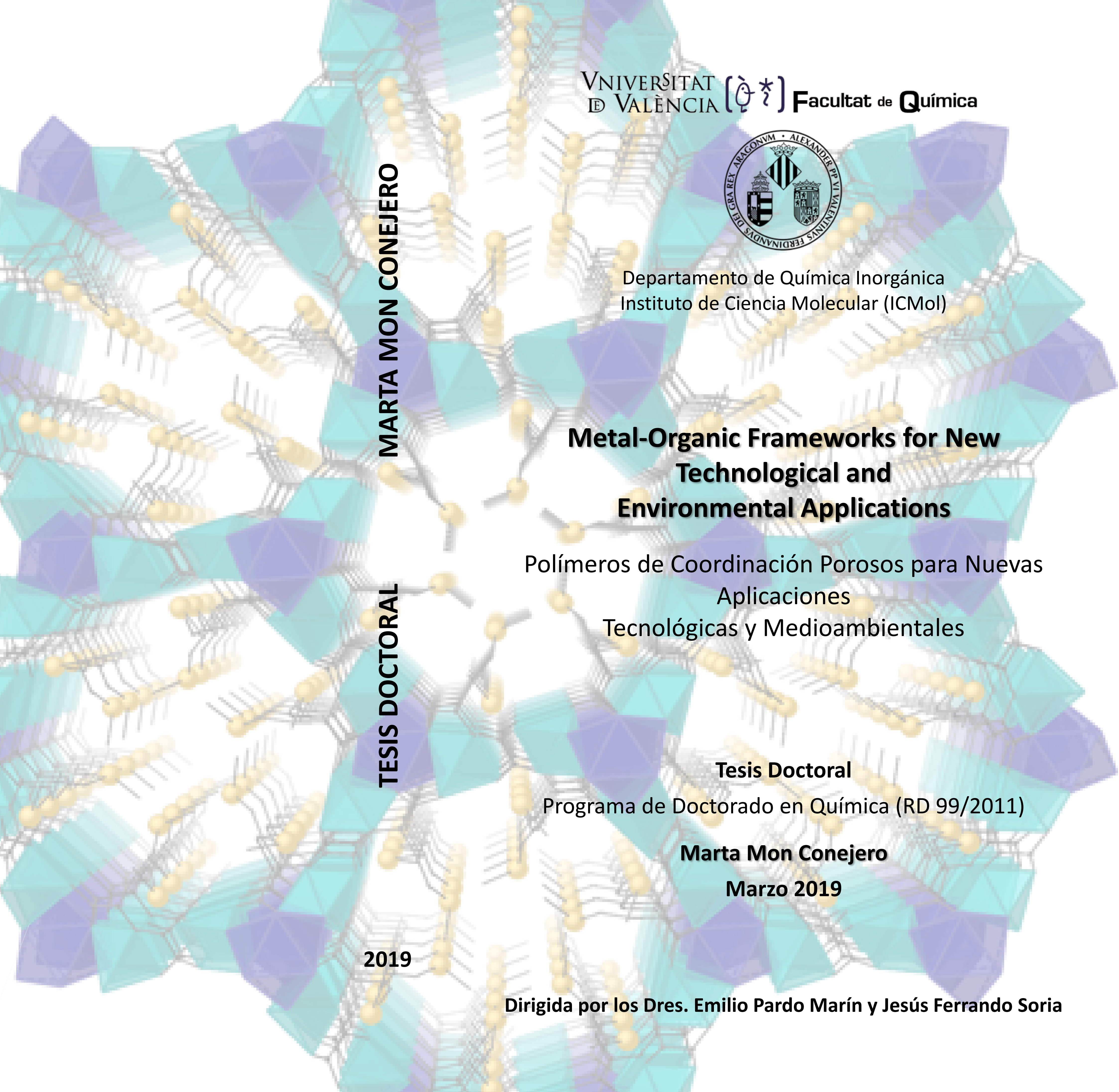




MARTA MON CONEJERO

TESIS DOCTORAL

2019



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Polímeros de Coordinación Porosos para Nuevas Aplicaciones Tecnológicas y Medioambientales

Tesis Doctoral

Programa de Doctorado en Química (RD 99/2011)

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CERTIFICA/N:

Que la memoria que presenta Dña. **Marta Mon Conejero**, titulada "***Metal-Organic Frameworks for New Technological and Environmental Applications***", corresponde al trabajo realizado bajo nuestra dirección en el Instituto de Ciencia Molecular y el Departamento de Química Inorgánica de la Universitat de València, para su presentación como Tesis Doctoral en el Programa de Doctorado en Química de la Universitat de València.

Y para que así conste, firmamos el presente certificado en Paterna, a 28 de febrero de 2019.

Fdo.: Dr. Emilio Pardo Marín

Fdo.: Dr. Jesús Ferrando Soria

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A mi familia y amigos

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Table of Contents

Abbreviations

MOFs	Metal-organic frameworks
CPs	Coordination polymers
PCPs	Porous coordination polymers
SBUs	Secondary building units
IUPAC	International Union of Pure and Applied Chemistry
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
IRMOFs	Isoreticular metal-organic frameworks
MIL	Materials of Institut Lavoisier
HKUST	Hong Kong University of Science and Technology
ZIFs	Zeolitic imidazolate frameworks
AIDS	Acquired immune deficiency syndrome
NMOFs	Nanoscale metal-organic frameworks
MR	Magnetic resonace
NCs	Nanoclusters
NPs	Nanoparticles
LLCT	Ligand-to-ligand charge transfer
LMCT	Ligand-to-metal charge transfer
MLCT	Metal-to-ligand charge transfer
LMOFs	Luminescent metal-organic frameworks
VOCs	Volatile organic compounds
SCO	Spin crossover
SMMs	Single-molecule magnets
SIMs	Single-ion magnets
SCM	Single-chain magnet
CSCMs	Chiral single chain magnets
MMCPs	Multifunctional magnetic coordination polymers
CSCMs	Chiral single chain magnets
SC to SC	Single-crystal to single-crystal
PSMs	Post-synthetic methods
PXRD	Powder X-ray diffraction
SCXRD	Single-crystal X-ray diffraction
EA	Elemental analysis
WHO	World Health Organization
IR	Infrared spectroscopy
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy
PAHs	Polycyclic aromatic hydrocarbons

AOPs	Advanced oxidation processes
PSD	Post-synthetic deprotection
PSP	Post-synthetic polymerization
PSI	Post-synthetic insertion
PSE	Post-synthetic exchange
SALI	Solvent-assisted linker incorporation
SALE	Solvent-assisted linker exchange
SACs	Single-atom catalysts
sMCs	sub-Nanometric metal clusters
QTM	Quantum tunneling relaxation of the magnetization
MTV-MOFs	multivariate-MOFs
SMCs	Supramolecular metallacyclic complexes
i.e.	*id est* (that is)
e.g.	*exempli gratia* (for example)
ed.	Editor
DMF	*N*,*N*-Dimethylformamide
DCB	1,2-Dichlorobenzene

Resumen/Abstract

Resumen

Esta tesis doctoral se acoge a la modalidad de “compendio de publicaciones”, de acuerdo con el reglamento sobre depósito, evaluación y defensa de la tesis doctoral de la Universidad de Valencia, ACGUV 266/2011, con última modificación el 31-X-2017. Cumpliendo con este reglamento, en esta sección se presenta un resumen global de la temática, los resultados más relevantes, así como las conclusiones extraídas de los mismos.

Introducción

El trabajo descrito en la presente memoria esta dentro del campo de la Ciencia de los Materiales y la Química de Coordinación, ya que se centra en el diseño racional de nuevos materiales, en concreto, polímeros de coordinación porosos (PCPs), también llamados MOFs (del inglés, *Metal-Organic Frameworks*), y su uso en diversas aplicaciones de alto interés tecnológico y/o medioambiental.

A pesar de que el interés de la comunidad científica en estos materiales empezó a principios de los años 90, sus fascinantes propiedades químicas y físicas han revolucionado la Ciencia de los Materiales, creciendo exponencialmente año tras año el número de MOFs reportados, así como el rango de aplicaciones de los mismos. Los MOFs, son una clase de materiales porosos cristalinos, constituidos por cationes o complejos metálicos discretos que se unen a través de ligandos puente mediante enlaces de coordinación. Su alta porosidad y cristalinidad, hace posible obtener grandes áreas superficiales y volúmenes de poro, y que puedan ser caracterizados mediante técnicas de difracción de rayos X. Además, su carácter modular y las infinitas combinaciones posibles entre ligandos orgánicos e iones/complejos metálicos inorgánicos, permite que puedan obtenerse una gran cantidad de estructuras distintas con composición, topología, y como consecuencia, propiedades físicas y químicas diseñadas a la carta (química reticular). Debido a estas características, los MOFs pueden tener aplicación en diversos campos, como adsorción y separación de gases, magnetismo, ferroelectricidad, transporte y liberación de fármacos, catálisis, etc.

A diferencia de los MOFs, los materiales porosos tradicionales (zeolitas, silicatos mesoporosos, óxidos metálicos o carbonos activos), tienen una composición química, tamaño de poro y funcionalidad limitada, por lo que no son tan versátiles como estos nuevos materiales. Esta versatilidad, ha hecho que los MOFs sean muy atractivos en las últimas décadas, dando lugar a numerosas publicaciones.

Objetivos

El objetivo principal de esta tesis doctoral es obtener nuevos polímeros de coordinación porosos, con el propósito de emplearlos para la captura o encapsulación de metales pesados (oro, mercurio o tierras raras) o especies orgánicas (diferentes drogas/medicamentos o colorantes), para adsorción de gases, así como para la síntesis *in-situ* de clústeres metálicos subnanométricos (sMCs, del inglés, *sub-Nanometric Metal Clusters*) de interés en catálisis, mostrando, con ello, la importancia que tienen este tipo de materiales en diferentes áreas tecnológicas.

Los MOFs desarrollados en esta tesis doctoral, tienen un doble interés. Por un lado, permiten reducir, hasta límites permisibles por la Organización Mundial de la Salud (OMS), la presencia de contaminantes en los ecosistemas acuáticos. Por otro lado, pueden emplearse como catalizadores heterogéneos para llevar a cabo reacciones de manera más sostenible.

En concreto, se han llevado a cabo los siguientes puntos:

1. Diseño y síntesis de nuevos MOFs, con poros de diferente tamaño, forma y grupos funcionales, empleando para ello diferentes proligandos oxamidato derivados de aminoácidos.
2. Modificación post-sintética tanto de los MOFs obtenidos, así como de otros sintetizados anteriormente por miembros del grupo, con el fin de mejorar o incorporar nuevas propiedades en ellos, o incluso formar nuevas especies dentro de sus canales, como clústeres metálicos subnanométricos.
3. Caracterización de los materiales mediante técnicas de: análisis elemental (AE), espectroscopia de infrarrojo (IR), análisis termogravimétrico (TG), microscopía electrónica de barrido (MEB), difracción de rayos X (DRX) de monocristal y polvo y adsorción de N_2 y CO_2.
4. Estudio de las propiedades y aplicaciones que poseen los materiales obtenidos. Algunas de ellas han sido evaluadas en colaboración con otros grupos de investigación.

Metodología sintética y MOFs obtenidos a partir de aminoácidos

Para obtener los MOFs que se recogen en esta tesis, hemos aprovechado la gran experiencia en química de coordinación que posee nuestro grupo de investigación, en concreto, en la química de compuestos tipo oxamato y oxamidato.

Entre las diferentes metodologías sintéticas existentes para obtener estos compuestos metal-orgánicos, hemos optado por la estrategia de emplear complejos que actúen como ligandos puente entre otros metales (en inglés, *"complex-as-ligand" approach*), la cual permite ganar control sobre la dimensionalidad y topología de las redes que se pretenden formar.

En primer lugar, se han sintetizado proligandos tipo oxamidato a partir de ésteres metílicos de aminoácidos enantiopuros, ya que pueden aportar a la estructura final quiralidad, biocompatibilidad, estabilidad al agua y una rica diversidad estructural. Los aminoácidos están constituidos por un grupo amino, un grupo carboxilo y una cadena lateral específica, que hace que se distingan unos de otros, determinando su identidad, así como sus propiedades. En concreto, se han empleado los derivados de *L*-metionina, *L*-serina, *L*-treonina y *L*-histidina, ya que poseen grupos funcionales diferentes en sus cadenas laterales (grupos tioéter, hidroxilo o imidazol), lo que permite obtener MOFs con poros funcionales de diferente naturaleza.

En segundo lugar, con estos proligandos se han obtenido complejos dinucleares de cobre altamente estables. En la **Tabla 1**, se resumen dichos complejos preparados a partir de los correspondientes proligandos.

Tabla 1. Proligandos oxamidato y complejos dinucleares de cobre obtenidos.

Aminoácido	Ligando	Complejo
L-Metionina	H_2Me_2-(S,S)-methox	$(Me_4N)_2\{Cu_2[(S,S)\text{-methox}](OH)_2\}\cdot 4H_2O$
L-Serina	H_2Me_2-(S,S)-serimox	$(Me_4N)_2\{Cu_2[(S,S)\text{-serimox}](OH)_2\}\cdot 5H_2O$
L-Treonina	H_2Me_2-(S,S)-threomox	$(Me_4N)_2\{Cu_2[(S,S)\text{-threomox}](OH)_2\}\cdot 4H_2O$
L-Histidina	H_2Me_2-(S,S)-hismox	$(Bu_4N)_2\{Cu_2[(S,S)\text{-hismox}](OH)_2\}\cdot 4H_2O$

Finalmente, para construir las redes tridimensionales se han utilizado estos complejos que actuaran como ligandos puente entre metales alcalinotérreos (Ca^{2+} y Sr^{2+}), a través de sus grupos carboxilato y grupos hidroxilo o moléculas de agua (en función del pH). De esta manera, mediante un proceso sintético sencillo y de bajo coste se ha obtenido una familia de MOFs estables en agua (**Tabla 2**), que poseen poros funcionales de diferente tamaño, forma y reactividad.

Tabla 2. Polímeros de coordinación porosos sintetizados.

Aminoácido	MOF	Grupo espacial / Sistema cristalino
L-Metionina	$\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}\cdot 16H_2O$ (**1**)	$P6_3$ / sistema hexagonal
	$\{Cu^{II}_4[(S,S)\text{-methox}]_2\}\cdot 5H_2O$ (**2**)	$P4_2$ / sistema tetragonal
L-Serina	$\{Ca^{II}Cu^{II}_6[(S,S)\text{-serimox}]_3(OH)_2(H_2O)\}\cdot 39H_2O$ (**3**)	$P6_3$ / sistema hexagonal
	$\{Sr^{II}Cu^{II}_6[(S,S)\text{-serimox}]_3(OH)_2(H_2O)\}\cdot 38H_2O$ (**4**)	
L-Treonina	$\{Sr^{II}Cu^{II}_6[(S,S)\text{-threomox}]_3(OH)_2(H_2O)\}\cdot 36H_2O$ (**5**)	$P6_3$ / sistema hexagonal
L-Histidina	$Ca^{II}_6\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 212H_2O$ (**6**)	$R3$ / sistema trigonal

En el caso de la *L*-metionina, a partir de su correspondiente complejo dinuclear de cobre se han obtenido dos MOFs diferentes, uno de ellos, utilizando un metal alcalinotérreo (**1**), como hemos indicado, y el otro, empleando una disolución acuosa ácida (**2**). Este último, que es homometálico se forma por unión directa de los dímeros de cobre a través de sus propios grupos carboxilato y presenta tres tipos de poros funcionales cuadrados, uno hidrofílico y dos hidrofóbicos, de aproximadamente 0.32, 0.34 y 0.4 nm, respectivamente. Sus poros están decorados con grupos tioéter muy flexibles, que se encuentran dispuestos de manera diferente en cada tipo de poro, lo cual afectará a la interacción entre las moléculas huésped y los canales del anfitrión (en inglés, *host-guest chemistry*).

Tanto el MOF de *L*-metionina obtenido con calcio (**1**), como los obtenidos con *L*-serina (**3** y **4**) y *L*-treonina (**5**) con calcio y/o estroncio, presentan canales hexagonales funcionales. En el caso de la *L*-serina y *L*-treonina, los poros poseen alrededor de 0.8-0.9 nm y están decorados con grupos hidroxilo, por lo que son hidrofílicos y proporcionan un entorno adecuado para alojar moléculas polares. En el caso del MOF sintetizado a partir de *L*-metionina, los poros son más pequeños (alrededor de 0.3 nm) y están decorados con grupos tioéter muy flexibles.

El MOF obtenido a partir de *L*-histidina (**6**), presenta un grupo espacial quiral diferente a estos últimos, además es un MOFs aniónico, que presenta dos tipos de cavidades, unas más pequeñas que son hexagonales o trigonales (de 0.5 y 0.4 nm, respectivamente) y otras más grandes que son pseudohexagonales (1.4 nm) y alojan $[Ca_2(\mu\text{-}H_2O)_2(H_2O)_8]^{4+}$, así como moléculas de agua.

Además de los MOFs mencionados, en esta tesis también se ha utilizado otro polímero de coordinación poroso, el cual fue sintetizado anteriormente por miembros del grupo a partir de un ligando oxamato. Para ello, utilizando la misma estrategia sintética mencionada, se prepararó el correspondiente complejo dinuclear de cobre y a partir de él se formó la red tridimensional, adicionando otro metal. En concreto, se ha empleado el MOF bimetálico de fórmula $Mg^{II}_2\{Mg^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\}\cdot 45H_2O$ ($Mg^{II}_4Cu^{II}_6$) [Me_3mpba^{4-} = *N,N'*-2,4,6-trimethyl-1,3-phenylenebis(oxamato)], con el objetivo de mejorar o incorporar nuevas propiedades en él, o incluso utilizarlo como plantilla para formar nuevas especies, ya que es un MOF aniónico muy robusto. La red aniónica $Mg^{II}_4Cu^{II}_6$ cristaliza en el grupo espacial *P*4/*mmm* del sistema tetragonal y presenta tres tipos de poro, uno cuadrado y dos octogonales (uno hidrofílico y otro hidrofóbico), los cuales están ocupados por los cationes que compensan la carga de la red, así como por moléculas de agua.

Estructura

La presente memoria se ha estructurado en cinco secciones, siendo la primera introductoria. En ella, se ha realizado una breve revisión histórica desde los polímeros de coordinación hasta los MOFs, detallando como las aportaciones de algunos científicos en el campo (Robson, Hoskins, Yaghi, Kitagawa, Férey, entre otros), así como los avances en cristalografía y la técnica de difracción de rayos X de monocristal, contribuyeron al desarrollo y estudio de estos materiales. A continuación, se muestra la clasificación de los compuestos de coordinación y la terminología empleada. Seguidamente, se describen las propiedades que los MOFs pueden presentar, haciendo hincapié en su porosidad, ya que es la característica que más interés ha despertado. Esto se debe a que su naturaleza porosa permite la difusión de especies en sus poros, presentando una fascinante química *host-*

guest, que puede ser modulada mediante el control del tamaño, forma y reactividad de los poros. Además, se indican algunas de sus aplicaciones, dando ejemplos de MOFs representativos que las poseen, así como describiendo, en cada caso, cuales son los factores determinantes que hacen que puedan emplearse con tales fines. Esta sección concluye, justificando la elección de la estrategia sintética utilizada, de manera que se muestran las ventajas que posee el uso de ligandos oxamato y oxamidato, así como la preparación de metaloligandos a partir de los cuales formar redes metal-orgánicas tridimensionales. Además, se hace una revisión de los compuestos obtenidos por los grupos de investigación pioneros en esta química, entre los que se encuentra nuestro grupo de investigación.

La segunda sección recoge los trabajos (artículos 1-7) sobre los MOFs sintetizados que son capaces de capturar contaminantes orgánicos o inorgánicos del agua. Cabe indicar, que esta sección contiene dos publicaciones (artículos 4 y 6) que no versan, de manera directa, sobre la captura de contaminantes en medios acuosos sino de las interacciones *host-guest* que se establecen entre una serie de medicamentos y los MOFs (artículo 4) y la separación de mezclas de lantánidos en medios no acuosos (artículo 6). Dichas publicaciones se han incluido en esta sección, ya que permiten elucidar las interacciones *host-guest* responsables de la captura de contaminantes. En la tercera sección se incluyen las publicaciones (artículos 8-9) en las que hemos empleado métodos post-sintéticos para dotar a los materiales de diferentes propiedades, como ferroeléctricas o de adsorción de gases. De este modo, se muestra como el uso de esta estrategia permite diseñar materiales para aplicaciones específicas. La cuarta sección contiene las publicaciones (artículos 10-12) en las que las modificaciones post-sintéticas se han utilizado, en concreto, para obtener MOFs con aplicación catalítica. Y, por último, en la quinta sección se recopilan las conclusiones de esta tesis.

Resultados

A continuación, se describen los principales resultados y conclusiones obtenidos para cada uno de los trabajos que se incluyen en esta memoria, los cuales están divididos en tres partes: MOFs para descontaminación de aguas, uso de métodos post-sintéticos en MOFs y MOFs para catálisis, correspondientes a las secciones II, III y IV, respectivamente.

MOFs para descontaminación de aguas

En el primer trabajo, llamado "*Selective Gold Recovery and Catalysis in a Highly Flexible Methionine-Decorated Metal-Organic Framework*" (*J. Am. Chem. Soc.* 2016, *138*, 7864-7867), se llevó a cabo la captura de sales de oro(III) y oro(I) para poder recuperarlas de medios acuosos. Para ello, aprovechando la gran afinidad que presenta este metal por los derivados de azufre, se utilizó el MOF derivado del aminoácido *L*-metionina (**1**), ya que posee, en sus poros, grupos tioéter ($-CH_2CH_2SCH_3$) muy flexibles y accesibles. Se evaluó, la selectividad, así como la cinética del proceso, donde el material mostró gran afinidad por dichas sales, incluso en presencia de otros cationes metálicos que se encuentran normalmente en desechos electrónicos. Los materiales obtenidos tras la captura de las especies de oro fueron caracterizados mediante cristalografía de rayos X de monocristal, y se estudió su actividad catalítica para llevar a cabo reacciones de hidroalcoxilación de alquinos, mostrando excelentes rendimientos. Además, se comprobó que las sales de oro pueden extraerse de los canales del MOF con ayuda de sulfuro de dimetilo, siendo el MOF reutilizable, lo cual es muy importante desde un punto de vista económico y ambiental.

En el segundo artículo, denominado "*Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF*" (*Angew. Chem. Int. Ed.* 2016, *55*, 11167-11172), se utilizó el mismo MOF derivado del aminoácido *L*-metionina (**1**), pero en este caso para capturar especies tóxicas de mercurio, dado que este metal también tiene gran afinidad por los átomos de azufre. Por tanto, se estudió la capacidad de afinidad y selectividad de este material por Hg^{2+} y CH_3Hg^+, mostrando una capacidad de adsorción de hasta 5 moléculas de Hg_2Cl_2 por unidad de fórmula, y en el caso de CH_3HgCl, de solo una molécula, dada su menor solubilidad y/o afinidad por los grupos tioéter. Estas moléculas quedaron inmovilizadas en las cavidades del MOF a través de interacciones S···Hg, observando mediante difracción de rayos X de monocristal, como las cadenas de tioéter, gracias a la gran flexibilidad que poseen, adoptan diferentes conformaciones en función de la especie capturada. Cabe destacar, que este material posee una capacidad de adsorción de estos contaminantes muy elevada, y es capaz de reducir las concentraciones de Hg^{2+} y CH_3Hg^+ de 10 ppm a valores de 6 y 27 ppb, respectivamente, los cuales están dentro de los límites permitidos en agua potable por la OMS. Además, la adsorción de estas especies es reversible, por lo que el material puede reutilizarse.

En la siguiente publicación, "*Fine-tuning of the confined space in microporous metal-organic frameworks for efficient mercury removal*" (*J. Mater. Chem. A* 2017, *5*, 20120-20125), también se evaluó la capacidad para capturar $HgCl_2$, pero en este caso con otro MOF derivado de *L*-metionina (**2**), el cual presenta poros funcionales cuadrados. Estos poros están decorados con grupos tioéter ($-CH_2CH_2SCH_3$), los cuales inmovilizan de manera muy eficiente dicho contaminante, formando un aducto de $HgCl_2S_2$ muy estable. Por tanto, este material, permite la captura selectiva, eficiente y rápida de $HgCl_2$ de medios acuosos, reduciendo su concentración de 10 ppm a menos de 2 ppb en unos 10 min, gracias a la combinación del tamaño y forma de sus canales, así como a las posiciones estratégicas que ocupan los grupos tioéter en ellos. El hecho de que este MOF pueda sintetizarse en escala de gramos, mediante un proceso sencillo, de bajo coste y medioambientalmente benigno, y que tenga una capacidad de captura tan elevada y rápida, lo convierte en uno de los materiales más efectivos para llevar a cabo la descontaminación de Hg^{2+} del agua. Además, también se estudió su capacidad para absorber gases como N_2, CO_2 y CH_4, así como mezclas de estos, mostrando diferencias en la adsorción, lo que hace que tenga potencial para ser utilizado para preparar membranas de separación.

En el cuarto trabajo, titulado "*Crystallographic snapshots of host-guest interactions in drugs@metal-organic frameworks: towards mimicking molecular recognition processes*" (*Mater. Horiz.* 2018, *5*, 683-690), se presenta la síntesis del MOF de $Ca^{II}Cu^{II}_6$ derivado del aminoácido *L*-serina (3), el cual posee poros funcionales decorados con grupos hidroxilo (-CH_2OH). La presencia de estos grupos funcionales dentro de los poros proporciona un entorno adecuado para llevar a cabo la captura de diferentes especies orgánicas. En concreto, en este trabajo, se estudió la capacidad del material para hospedar moléculas de diferente tamaño y naturaleza química en acetonitrilo, como son: dos vitaminas (vitamina C y vitamina B6), un antidepresivo (bupropión) y una hormona femenina (17-β-estradiol). Gracias a la gran estabilidad del MOF tras la captura de dichas especies y su gran cristalinidad, mediante cristalografía de rayos X de monocristal, se pudo observar como los grupos hidroxilo son capaces de establecer interacciones por puentes de hidrógeno, que son específicas para cada una de estas moléculas, actuando como sitios de reconocimiento molecular. Este hecho, permitió obtener información muy valiosa sobre las interacciones *host-guest*, y por tanto, ayudar a entender un poco mejor los procesos de reconocimiento molecular.

En el quinto artículo, llamado "*Efficient Capture of Organic Dyes and Crystallographic Snapshots by a Highly Crystalline Amino Acid-Derived Metal-Organic Framework*" (*Chem. Eur. J.* **2018**, *24*, 17712-17718), se empleó el mismo MOF derivado del aminoácido *L*-serina (3), pero en este caso para capturar colorantes orgánicos que pueden estar presentes en aguas residuales de diferentes industrias, como son: pyronina Y, auramina O, azul de metileno o verde brillante. Este MOF mostró que es capaz de adsorber más del 90 % del contenido de dichos colorantes en agua, incluso en concentraciones muy bajas (10 ppm), similares a las que normalmente se encuentran en las aguas residuales industriales. Aunque ya se han publicado otros MOFs que presentan dicha capacidad, en la mayoría de los casos la captura se da mediante procesos de intercambio iónico, lo cual limita su uso, ya que solo sería posible capturar los colorantes de carga complementaria al material utilizado. Sin embargo, en el MOF derivado de *L*-serina, los cuatro colorantes residen en los poros por interacciones débiles C-H···O o por puentes de hidrógeno, e incluso puede llevarse a cabo su captura de manera simultánea.

En el sexto trabajo, denominado "*Lanthanide Discrimination with Hydroxyl-Decorated Flexible Metal-Organic Frameworks*" (*Inorg. Chem.* **2018**, *57*, 13895-13900), se describe la síntesis de los MOFs $Sr^{II}Cu^{II}_6$ derivados de los aminoácidos *L*-serina (4) y *L*-treonina (5) y se evalúa su capacidad para capturar y separar diferentes sales de lantánidos. Los poros de ambos MOFs están decorados con grupos hidroxilo (-CH_2OH y -$CH(OH)CH_3$, respectivamente), proporcionando entornos funcionales capaces de interactuar con las tierras raras. En concreto, se estudió la captura de $LaCl_3$, $CeCl_3$, $DyCl_3$ y $ErCl_3$ en acetonitrilo, consiguiendo resolver las estructuras cristalinas de los MOFs en cada caso, lo cual mostró como los lantánidos están dispuesto de manera diferente dependiendo de la naturaleza del MOF y del lantánido. Además, estos materiales separan mezclas equimolares de dichas sales de manera diferente, en función del radio del lantánido y su afinidad por los grupos hidroxilo de los poros, así como de la flexibilidad y disposición de estos.

En el último trabajo de esta sección, denominado "*Metal-organic framework technologies for water remediation: towards a sustainable ecosystem*" (*J. Mater. Chem. A* **2018**, *6*, 4912-4947), se hace una revisión bibliográfica de los últimos logros conseguidos utilizando MOFs como adsorbentes de contaminantes orgánicos e inorgánicos, que se encuentran normalmente presentes en los ecosistemas acuáticos. Además, se intenta dar una idea de las diferentes estrategias sintéticas empleadas para obtener MOFs que puedan utilizarse para capturar tales especies.

Uso de métodos post-sintéticos en MOFs

En el octavo trabajo, titulado "*Postsynthetic Approach for the Rational Design of Chiral Ferroelectric Metal-Organic Frameworks*" (*J. Am. Chem. Soc.* **2017**, *139*, 8098-8101), se presenta una estrategia post-sintética para llevar a cabo el diseño racional de materiales ferroeléctricos. Estos materiales se caracterizan por mostrar, por debajo de cierta temperatura, polarización espontánea en ausencia de un campo eléctrico externo, y su dirección puede revertirse aplicando un campo eléctrico. Son materiales que atraen un gran interés, ya que poseen muchas aplicaciones tecnológicas importantes, incluyendo el almacenamiento de datos y energía. La estrategia propuesta consiste, en primer lugar, en el diseño de un MOF que posea un grupo espacial adecuado para tal fin. En concreto, se describe la síntesis del MOF derivado del aminoácido *L*-histidina (**6**), el cual es un MOF aniónico con un grupo espacial quiral no centrosimétrico, que posee cationes calcio alojados en sus poros, compensando la carga de la red. Para obtener un material ferroeléctrico, además de que el MOF presente un grupo espacial adecuado, las moléculas huésped deben tener gran polaridad. Por ello, en segundo lugar, se llevó a cabo la modificación post-sintética del MOF, intercambiando los iones calcios por moléculas polarizables como $CH_3NH_3^+$. De esta manera, se consiguió obtener un material que presenta comportamiento ferroeléctrico por debajo de 260 K.

En la noveno publicación, denominada "*A post-synthetic approach triggers selective and reversible sulphur dioxide adsorption on a metal-organic framework*" (*Chem. Commun.* **2018**, *54*, 9063-9066), se han empleado los métodos post-sintéticos para dotar a un material de capacidad para adsorber SO_2. La principal fuente de emisión a la atmósfera de este gas es la quema de combustibles fósiles, siendo uno de los causantes de la famosa lluvia ácida, dado que reacciona con el vapor de agua produciendo ácido sulfúrico. Esto hace, que el descubrimiento de nuevos materiales que permitan la desulfuración del aire, de manera económica y sostenible, suponga un gran avance. Contribuyendo con tal fin, hemos utilizado el método de intercambio iónico para obtener un nuevo MOF con cationes bario alojados en sus poros, ya que los iones bario poseen afinidad por las moléculas de SO_2. La obtención de este material se llevó a cabo en dos pasos utilizando el MOF $Mg^{II}_4Cu^{II}_6$. El primer paso consistió en transmetalar los iones Mg^{II}, tanto de los canales como de la red, por iones Ni^{II}, para obtener el MOF de fórmula, $Ni^{II}_2\{Ni^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\}\cdot 54H_2O$ ($Ni^{II}_4Cu^{II}_6$). Esto permitió obtener un MOF mucho más robusto, lo cual fue previamente demostrado por miembros del grupo. Y el segundo paso, consistió en el intercambio de los iones Ni^{II} alojados en los poros por iones Ba^{II}, obteniendo así un MOF capaz de adsorber SO_2 de manera selectiva y reversible.

MOFs para catálisis

En los artículos décimo y undécimo, titulados *"Isolated Fe(III)-O Sites Catalyze the Hydrogenation of Acetylene in Ethylene Flows under Front-End Industrial Conditions"* (*J. Am. Chem. Soc.* 2018, *140*, 8827-8832) y *"Stabilized Ru[(H₂O)₆]³⁺ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope"* (*ACS Catal.* 2018, 8, 10401-10406), también se emplearon modificaciones post-sintéticas, pero en estos casos, para incorporar en los canales de un MOF especies que puedan ser activas en catálisis. Para ello, se utilizó el MOF aniónico $Ni^{II}_4Cu^{II}_6$, en el cual se intercambiaron los iones Ni^{II} alojados en los poros, y que actúan de contracationes para compensar la carga de la red, por especies de Fe^{III} y Ru^{III}. Estas especies, son reactivas e inestables, sin embargo, el hecho de ser incorporadas en las cavidades del MOF dio lugar a su estabilización mediante diferentes interacciones con la red. Gracias a la alta robustez y cristalinidad de estos MOFs, sus estructuras pudieron ser resueltas mediante difracción de rayos X en monocristal, permitiendo la caracterización de las especies huésped. Los estudios de actividad catalítica demostraron que ambos materiales pueden emplearse como eficientes catalizadores heterogéneos, en el caso del Fe^{III} para llevar a cabo hidrogenaciones de acetileno en condiciones similares a las industriales, y en el caso de Ru^{III} para catalizar la iminación de alcoholes, a pH ligeramente ácido y en atmósferas con bajo contenido de oxígeno.

En el último trabajo que se presenta en esta tesis, nuestro esfuerzo se ha centrado en el uso de MOFs como "nanoreactores" para llevar a cabo la síntesis de clústeres metálicos subnanométricos, con el objetivo de obtener catalizadores heterogéneos con gran actividad catalítica. Para ello, hemos usado una estrategia consistente en dos pasos post-sintéticos consecutivos. En primer lugar, se lleva a cabo la incorporación en los poros del MOF de la sal metálica elegida y, posteriormente, tiene lugar la reducción de los iones metálicos insertados. Este procedimiento representa un gran avance respecto a los métodos usados comúnmente para la obtención *in-situ* de clústeres metálicos, ya que el hecho de que los iones metálicos estén confinados dentro de los canales del MOF e incluso restringidos en número, ofrece la posibilidad única de ganar control en la formación de estas especies metálicas tan pequeñas.

Por lo que en la décimo segunda publicación, titulada *"The MOF-driven synthesis of supported palladium clusters with catalytic activity for carbene-mediated chemistry"* (*Nat. Mater.* 2017, *16*, 760-766), se ha utilizado el MOF aniónico $Ni^{II}_4Cu^{II}_6$ como "nanoreactor" para sintetizar clústeres de Pd. Para ello, se insertaron iones $[Pd^{II}(NH_3)_4]^{2+}$ dentro de los poros del MOF, intercambiándolos por los Ni^{II}, y posteriormente, se llevó a cabo su reducción con $NaBH_4$. Esta estrategia permitió obtener clústeres de $Pd_4^{0/+1}$ de valencia mixta, estabilizados y organizados homogéneamente dentro de los canales del MOF. El material resultante ha demostrado ser capaz de catalizar de manera muy eficiente, reacciones mediadas por carbeno como la reacción de Buchner y la dimerización de diazocompuestos.

En estos trabajos, la doctoranda ha llevado a cabo, la síntesis de los ligandos, complejos dinucleares de cobre y MOFs a partir de aminoácidos, así como la obtención de los nuevos materiales mediante las correspondientes modificaciones post-sintéticas. Además, ha realizado la caracterización física de los materiales obtenidos mediante IR, RMN, difracción de rayos X de polvo, adsorción de N_2 y CO_2 y microscopía electrónica de barrido. Sin embargo, la resolución de las estructuras mediante difracción de rayos X de monocristal, estudios de ferroelectricidad, de adsorción de otros gases diferentes a los indicados y estudios de actividad catalítica, han sido llevados a cabo por el resto de coautores.

Abstract

This thesis is presented as "compendium of publications", in accordance with the regulation on deposit, evaluation and defense of the doctoral thesis of the University of Valencia, ACGUV 266/2011, as last amended on 31-X-2017.

The work described in this report is within the field of Materials Science and Coordination Chemistry, since it focuses on the rational design of new materials, specifically, porous coordination polymers (PCPs), also called metal-organic frameworks (MOFs), and its use in diverse applications of high technological and/or environmental interest.

The main objectives of this thesis are to obtain new porous coordination polymers, and the study of their properties for the capture or encapsulation of heavy metals (gold, mercury or rare earths) or organic species (different drugs or dyes), for gas sorption, as well as for the *in-situ* synthesis of sub-nanometric metal clusters (sMCs) of interest in catalysis. Thus, we have shown the importance of this type of materials in different technological areas.

The MOFs developed in this doctoral thesis have a two-fold relevance. On the one hand, they allow reducing the presence of pollutants in aquatic ecosystems, to limits that are permissible by the World Health Organization (WHO). On the other hand, they can be used as heterogeneous catalysts to carry out reactions in a more sustainable way.

In particular, the following points have been carried out:

1. Design and synthesis of new MOFs, with pores of different size, shape and functional groups, using for this purpose diverse oxamidate proligands derived from amino acids.
2. Post-synthetic modification of the obtained MOFs, as well as of others previously reported by members of the group, in order to improve or introduce new properties in them, or even to synthesize new species within their channels, such as sub-nanometric metal clusters.
3. Characterization of the materials using techniques such as: elemental analysis (EA), infrared spectroscopy (IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD) and N_2 or CO_2 adsorption.
4. Study of the properties and applications of the resulting materials. Some of them have been evaluated in collaboration with other research groups.

The present thesis has been structured in five sections, being the first introductory. Where, a brief historical review has been made from the coordination polymers to the MOFs, detailing how the contributions of some scientists in the field (Robson, Hoskins, Yaghi, Kitagawa, Férey, among others), as well as the advances in crystallography and the single-crystal X-ray diffraction technique contributed to the development and study of these materials. Then, the classification of the coordination compounds and the terminology used is shown. Next, the properties that MOFs can present are described, emphasizing their porosity, since it is the feature that has aroused the most interest. This is because its porous nature allows the diffusion of species in its pores, presenting a fascinating host-guest chemistry, which can be modulated by controlling the size, shape and reactivity of the pores. Furthermore, some of their applications are described, giving examples of representative MOFs that possess them, as well as showing, in each case, which are the determining factors that make them usable for such purposes. This section concludes justifying the choice of the synthetic strategy employed, so that the advantages of using oxamate and oxamidate ligands are shown, as well as the preparation of metalloligands to form 3D MOFs. In addition, a review is made of the compounds obtained by pioneering research groups working in this chemistry, among which it is our research group.

The second section includes the works (articles 1-7) on the synthesized MOFs that are capable of capturing organic or inorganic contaminants from water. It should be noted that this section contains two publications (articles 4 and 6) that do not directly concern the capture of pollutants in aqueous media, but rather the host-guest interactions that are established between a series of drugs and MOFs (article 4) and the discrimination of a mixture of lanthanides in non-aqueous media (article 6). These publications have been included in this section, since they allow elucidating the host-guest interactions responsible for the capture of pollutants. The third section includes publications (articles 8-9) in which post-synthetic methods (PSMs) have been used to provide materials with different properties, such as ferroelectric or gas sorption. In this way, it is shown how the use of this strategy allows designing materials for specific applications. The fourth section contains the publications (articles 10-12) in which post-synthetic modifications have been used, in particular, to obtain MOFs with catalytic application. Finally, in the fifth section the conclusions of this thesis are collected.

I.

Introduction

I. Introduction

Over the last two decades, the interest in metal-organic frameworks (MOFs),[1-5] –also known as porous coordination polymers (PCPs)– has grown exponentially as a result of the quantity of high-dimensional structures with different compositions, topologies and chemical and physical properties that these crystalline porous materials may show. Their structures are based on single metal ions or polynuclear metal clusters (also known as secondary building units, SBUs) linked by a wide variety of organic ligands, through coordination bonds, to form infinite high-dimensional networks. In addition, the rich variety of organic ligands and metal ions allows designing networks with different pore sizes and shapes and surface functionality. Such synthetic control also allows to synthesize the so-called multifunctional materials,[6-11] in which two or more physical/chemical properties can be integrated in the compounds. Overall, synthetic strategies for the design of MOFs embrace different disciplines such as coordination chemistry, supramolecular chemistry, reticular chemistry, materials science and crystal engineering.

Going back a little into history, the emergence of MOFs at the end of last century had a great impact and constituted a new family on the field of porous materials.[12,13] This research was driven by the research groups of Robson and Hoskins[14,15] –which initially named them PCPs– and later by Yaghi,[16] Ferey,[17] Kitagawa[18] and others[19-22], the first of which coined them as MOFs. Much of the initial enthusiasm over this class of solids came from their crystallinity and porosity and thus, an extremely high capacity to capture gases (*e.g.*, N_2, H_2, CH_4, CO_2).[23-25] Currently, a lot of studies of MOFs are still focused on the gas storage and separation properties of these materials.[26,27] Besides, this notable interest in gas uptake, other potential applications[28] of MOFs have flourished in areas such as magnetism,[11] ferroelectricity,[29] conductivity,[30] catalysis,[31-33] luminescence[34,35] and biotechnology.[36,37] Moreover, they have emerged as very versatile materials as templates for the growth of nanoparticles or for constructing small metal clusters,[38-40] acting thus as hosts for a wide variety of guest molecules due to their large functional channels/pores.

I.1. From Coordination Polymers to Metal-Organic Frameworks

The beginning of modern coordination chemistry is attributed to Alfred Werner with the publication "Contribution to the Constitution of Inorganic Compounds" in 1893.[41] In fact, Werner played such an important and extraordinaire role in coordination chemistry that his name is still used in the field. So, coordination compounds, particularly metalammines, are still colloquially called Werner complexes.[42] Werner won the first Nobel Prize in Inorganic Chemistry in 1913.

On the basis of Werner work, the structural concept of framework/network in coordination chemistry was demonstrated in 1897 by Hofmann and Küspert.[43] They obtained the first inorganic clathrate compound with the composition $[Ni(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$, belonging to the latter-known family of Hofmann clathrates, with the general formula $M(NH_3)_2M'(CN)_4\cdot 2G$, where M is a six-coordinate and M' a four-coordinate divalent metal ion, and G is an aromatic guest molecule.[44]

According to the International Union of Pure and Applied Chemistry (IUPAC), a coordination polymer is "a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions"[45] and a coordination compound is "any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of atoms or groups of atoms, each of which is called a ligand".[46] In this connection, while the chemical foundation of coordination polymers dated back to the end of the 19th century, the term "coordination polymer" was first used by Y. Shibata in 1916 (founder of coordination chemistry in Japan and co-worker of Werner),[47] to describe dimers and trimers of several cobalt(II) ammine nitrates. However, it is considered that it appeared for the first time published by J. Bailar, in 1963, to describe bis-(β-diketone)-beryllium complexes,[48] which is known as the "Father of Coordination Chemistry" in the United States. Since then, the term of coordination polymer was in continuous use in the scientific literature, but there was no way to demonstrate the infinite nature of the frameworks until the improvement of single-crystal X-ray crystallography.

For example, long time before Werner's work, between 1704 and 1707, a three-dimensional coordination framework, named as Prussian Blue, was discovered by Diesbach and Dippel in a laboratory in Berlin. However, it was not identified until 1977 as coordination polymer,[49] when its structure was determined by X-ray diffraction techniques. Prussian Blue, of formula $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot xH_2O$ (x = 14-16), is a mixed valence compound with a cubic structure, in which alternating octahedral sites of Fe^{II} and Fe^{III} ions are linked through cyanide ligands, where carbon and nitrogen are connected to Fe^{II} and Fe^{III}, respectively (**Figure I.1**).

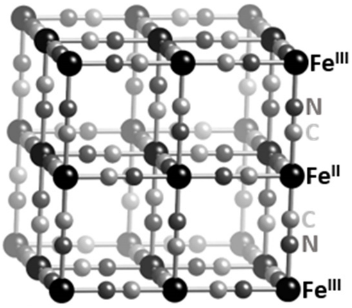


Figure I.1. Prussian Blue structure. Adapted from ref. 15.

The structural characterization of the so-called Hofmann clathrate, $[Ni(NH_3)_2(Ni(CN)_4]\cdot 2C_6H_6$, was also difficult and the structure remained unclear for almost 60 years. X-ray analysis was not carried out until 1949 by Powell and Rayner.[50] It consists of two-dimensional layers of alternating octahedral and square planar Ni^{II}, linearly connected through four CN^- moieties (**Figure I.2**). The terminal NH_3 ligand is axially bound and points towards the adjacent layer, thus forming a cavity that can encapsulate benzene molecules. Years later, this compound was modified, by Ywamoto's group, replacing the hexacoordinate Ni^{II} with other divalent ions such as Mn^{II}, Zn^{II}, Cd^{II}, and Cu^{II}, and the ammine with other ligands.[51,52] They introduced ethylenediamine (en) into these types of networks, which enabled the formation of an organic bridge between adjacent layers to make a three-dimensional host lattice.[53]

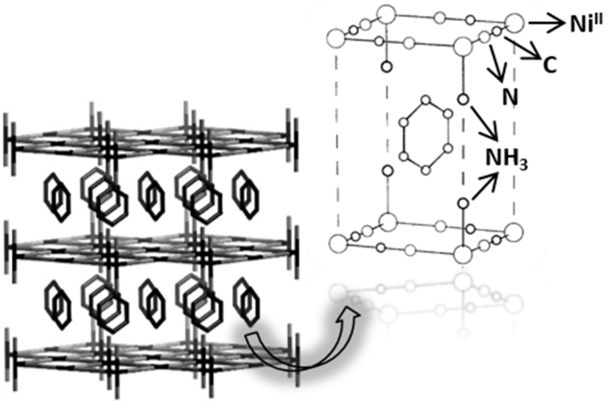


Figure I.2. Hofmann clathrate structure and environment of one benzene molecule. Adapted from ref. 15.

The first crystal structure of a three-dimensional network appeared in 1959,[54] when Saito and co-workers, trying to get information about the mechanism of cuprous ion dyeing of polyacrylonitrile fibers, crystallized the compound bis(adiponitrilo)copper(I) nitrate, $[Cu(NC\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CN)_2]NO_3$.[54-56] The family of bis(alkylnitrilo)copper(I) structures consists of tetrahedral $Cu(\text{-}CN)_4$ units connected through organic moieties with different length and the NO_3^- anions occupying its voids. Depending on the length and conformation of the organic moieties, they obtained one-[56], two-[55] or three-dimensional[54] compounds.

In the bis(adiponitrilo)copper(I) nitrate, the copper atoms are surrounded by four nitrogen atoms and each adiponitrile molecule is linked to two different copper atoms. Thus, the copper atoms and the ligand molecules construct a three-dimensional four-connected network[54] (**Figure I.3b**), in which all the copper atoms are arranged on a distorted diamond lattice (**Figure I.3a**), in accordance with the geometrical basis of crystal chemistry reported by A. F. Wells in 1954.[57]

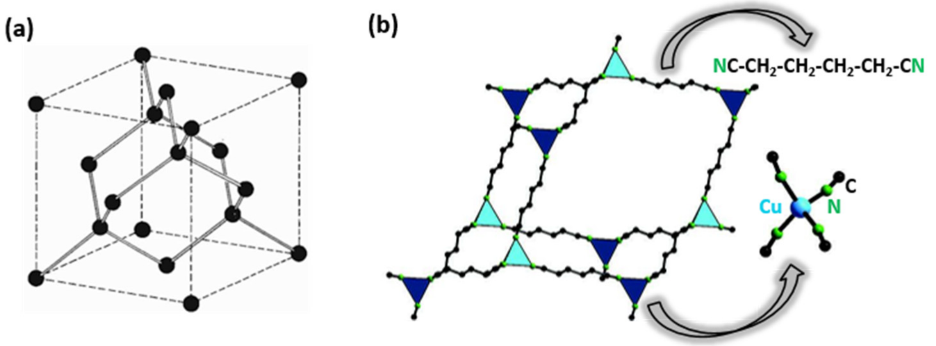


Figure I.3. (a) Diamond lattice and (b) three-dimensional structure of [Cu(adiponitrilo)$_2$]NO$_3$. Adapted from ref. 58.

Between the end of 1980 and the beginning of 1990, the field made an important leap forward due to the significant works of Robson, Hoskins and co-workers.[14,59-61] They applied the concepts of Wells, which described crystal structures in terms of networks,[62] in the design of new coordination polymers. In line with this idea, these authors suggested that materials with interesting properties such as porosity and catalysis could be designed.

One of the most remarkable contributions of Robson and Hoskins was to obtain an infinite, non-interpenetrated, cationic framework, of formula [Cu(TCTPM)]$^+$.[59] This was obtained by combining the tetrahedral single-metal building unit Cu(-CN)$_4$ together with the tetrahedral organic linker 4,4',4'',4'''-tetracyanotetraphenylmethane (TCTPM).

Following this approach, other groups in the field have made significant contributions.[16-22] Thus, different families of compounds could be obtained by using several multivalency metallic centers and multifunctional ligands, which led to specific novel structural topologies. This effort provided the tools for a conscious design and synthesis of extended 3D networks with controlled structure,[63,64] allowing the understanding of different synthetic factors on the final structure, porosity and chemical functionality of the assembled species.

In 1995, Omar M. Yaghi introduced, for the first time, the term metal-organic frameworks (MOFs), when he published the copper complex of formula Cu^I(4,4'-bpy)$_{1.5}$NO$_3$(H$_2$O)$_{1.25}$ (4,4'-bpy = 4,4'-bipyridine),[16] which exhibited extended metal-organic interactions resulting in a diamond-like structure (**Figure I.4**). Its X-ray structure revealed an extended cationic framework with rectangular channels filled by nitrate ions. He showed that the nitrates ions within the channels could be exchanged by other anions such as SO$_4^{2-}$ or BF$_4^-$, demonstrating the accessibility of the channels and –together with S. Kitagawa–introducing somehow the term “host-guest” chemistry into the MOFs field. [13,65] Since then, many compounds in this category have been synthesized and characterized crystallographically.[66]

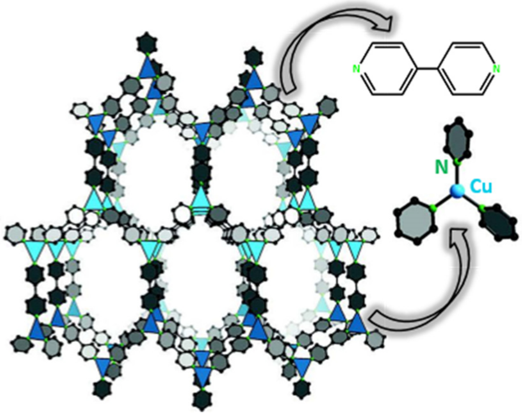


Figure I.4. Structure of [Cu^I(4,4’-bpy)$_{1.5}$NO$_3$]. Adapted from ref. 58.

I.2. Classification for Coordination Compounds

Given that, coordination polymers (CPs) and metal-organic frameworks (MOFs) are used in many areas of applied science and engineering it was important to establish a classification of the compounds in order to use a suitable terminology. As a result, a group of researchers in the field was commissioned by International Union of Pure and Applied Chemistry (IUPAC) with the task of defining a suitable terminology. In 2012, the authors presented a classification of solid-state coordination chemistry (**Figure I.5**).[45,67]

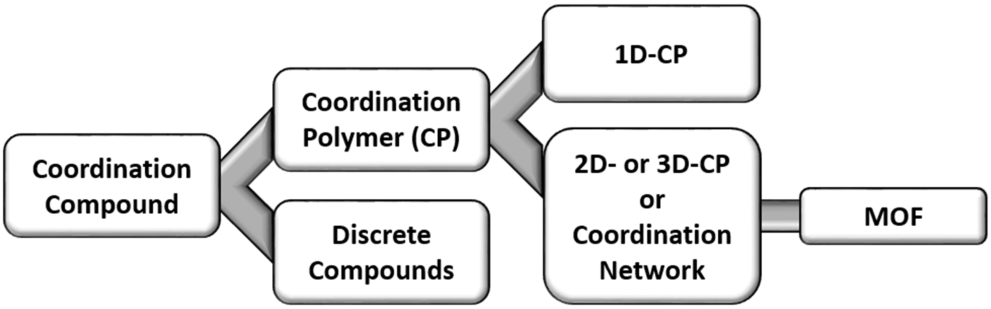


Figure I.5. Classification of coordination polymers and metal-organic frameworks.[67]

According to the IUPAC, a coordination network is a coordination compound extending, through repeating coordination entities, in one dimension (1D) –that may have cross-links between two or more individual chains, loops, or spiro-links– or a coordination compound extending through repeating coordination entities into two (2D) or three dimensions (3D).[45] On the other hand, a MOF, is a coordination network with organic ligands containing potential voids.[45] Therefore, coordination networks are a subset of CPs, and MOFs, a further subclass of coordination networks. As mentioned before, a coordination polymer is a compound with repeating coordination entities extending into an infinite array where the structure is defined by coordination bonds. For this reason, molecular species linked only by hydrogen bonding can be considered as examples of molecular compounds instead of coordination polymers.

Discrete compounds (**Figure I.6**) such as macrocycles,[68,69] cages[68,70] and capsules[71,72] among others, are excluded from the CP definition. However, the design and chemistry may be similar, except for the use of a convergent or divergent ligand building block. The first case will form a metallosupramolecule, while the second one will generate a CP.[15]

One-, two- and three-dimensional (1D, 2D and 3D) networks can be found within coordination polymers (**Figure I.7**). A structure linked by coordination bonds in one direction and supramolecular interactions (such as hydrogen bonding, π-π stacking and van der Waals) in two other directions is a 1D-coordination polymer (1D-CP). While a structure linked by coordination bonds in two directions and supramolecular interactions in another direction is a 2D-coordination polymer (2D-CP). In turn, those linked by coordination bonds in three directions are 3D-coordination polymers (3D-CPs).[74]

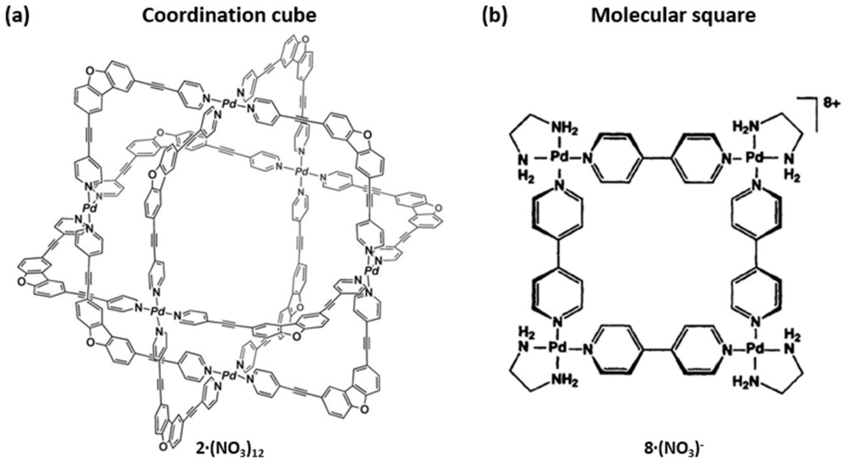


Figure I.6. Examples of discrete compounds: (a) M_6L_{12} coordination cube formed from pyridine-based bridging ligand and $Pd(NO_3)_2$;[72] (b) a molecular square, $[(en)Pd(4,4'\text{-bpy})]_4(NO_3)_8$, formed from 4,4'-bipyridine and $[Pd(en)(NO_3)_2]$.[73]

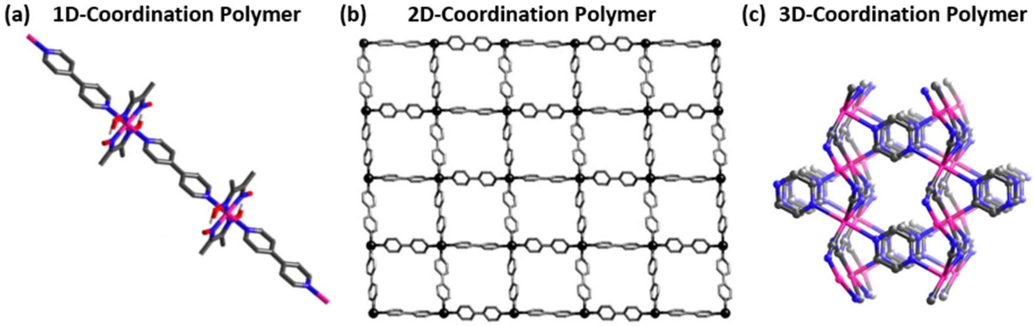


Figure I.7. (a) 1D-CP formed by the treatment of 4,4'-bpy with $Co(dimethylglyoximate)_2$,[45] (b) 2D-CP constructed from $ZnSiF_6$ and 4,4'-bpy;[75] (c) 3D-CP obtained from $Cd(CN)_2$ and pyrazine (pz).[76] Adapted from ref. 15 and 45.

Finally, it is worth mentioning that as the definition of MOFs implies, they should contain potential voids, but no physical measurements of porosity or other properties are demanded.

I.3. Properties and Applications of Metal-Organic Frameworks

I.3.1. Porosity in MOFs

Many different classes of porous molecular crystals and extended solids have been studied since Werner's work on coordination complexes,[77] but none of them showed to have permanent porosity until 1990s.[58,64,66,78]

MOFs structures are constructed by linking metal-containing units (secondary building units, SBUs) with organic linkers, using strong bonds to create crystalline frameworks with voids.[79,80] Therefore, they were suggested to have the potential to be permanently porous, as, for example, zeolites.

In the present context, the adjective porous is inappropriate for frameworks in which the included solvent molecules cannot be removed or exchanged without loss of framework integrity (irreversible loss of crystallinity). In other words, the structure must be preserved after removal of solvent "guest" from the cavities.

The most common method for examining that a framework exhibits permanent porosity is the measurement of reversible gas sorption isotherms at low pressures and temperatures. There are six types of representative adsorption isotherms that reflect the relationship between porous structure and sorption type.[81] It is based on an earlier classification by Brunauer, which had five types of isotherms.[82] Although these measurements were often used to confirm and study microporosity in crystalline zeolites and related molecular sieves,[83,84] such studies were not started to apply in MOFs chemistry until 1997, when Kondo, Kitawaga and collaborators (Kyoto University, Japan) carried out gas sorption experiments (CH_4, N_2 and O_2) on the 3D-structures of formula $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4](H_2O)_x\}_n$ (M = Co, Ni or Zn).[64] They showed that this metal-organic extended network maintained their structure without guests in the pores. However, since the experiments were carried out at high pressures (1-36 atm), they could not determine the surface area and pore volume.

One year later, Yaghi reported the first proof of permanent porosity of MOFs by measurement of nitrogen and carbon dioxide isotherms under low pressure on $Zn(BDC)(DMF)(H_2O)$ (BDC^{2-} = 1,4-benzenedicarboxylate) (**Figure I.8**).[78] This allowed the full characterization of the microporosity (determination of the surface area and pore size/volume) of this carboxylate-based framework, nowadays known as MOF-2.

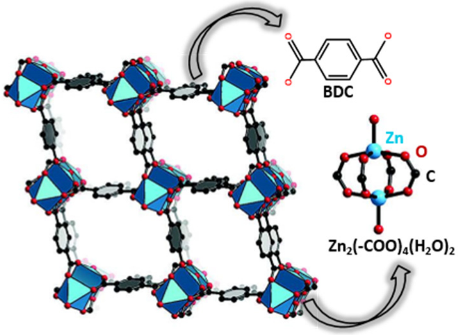


Figure I.8. View of structure of MOF-2. Adapted from ref. 58.

Within this context, in 1998, Kitagawa and Kondo suggested a classification of porous coordination compounds in three groups, which they named "first, second and third generations" (**Figure I.9**).[12,65]

- The first-generation materials are unstable on guest removal. So, they show an irreversible collapse of their frameworks upon the loss of guest molecules, such as Robson's CPs for instance.[14]

- The second-generation materials must have robust and rigid frameworks, since they maintain the crystallinity without any guest molecules in the pores. It might be said that this generation started in 1995, when the term metal-organic frameworks appeared.[16,63]

- The third-generation materials exhibit flexible and dynamic structures. They respond to chemical or physical external stimuli (pressure, light, electric field, guest molecule, among others)[85] changing their channels or pores reversibly. These materials introduced the terms flexibility and adaptability.[86] They have been widely studied since the beginning of the 2000s.[87]

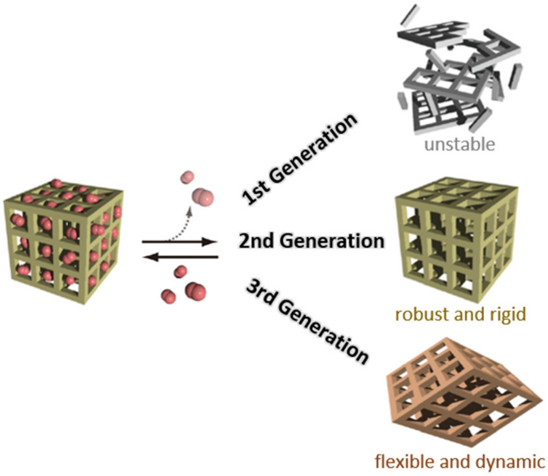


Figure I.9. Classification of crystalline coordination polymers having porous structures as proposed by S. Kitagawa. Adapted from ref. 86.

A major advance –related to porosity in MOFs– came in 1999 when MOF-5, well-known today and with formula $Zn_4O(BDC)_3(DMF)_8(C_6H_5Cl)$ (**Figure I.10**), was reported.[88] The popularity of this structure is due to the fact that it presents a structure with higher surface area and pore volume than most porous crystalline zeolites, together with an easy and versatile preparation. It was the first MOF based on linking octahedral zinc acetate building units, $Zn_4O(\text{-}COO)_6$, with six chelating 1,4-benzenedicarboxylate (BDC^{2-}) units to give a cubic framework.

Later, in 2002, it was reported that MOF-5 has a modular structure, and 16 isoreticular frameworks (IRMOF-1 to IRMOF-16) were synthesized by changing the length and functionality of the linkers (**Figure I.10**), and thus, the concomitant void space.[89] The open space in one of these isoreticular frameworks (IRMOF-16) represented up to 91.1% of the crystal volume and their homogeneous periodic pores could vary from 3.8 to 28.8 Å without changing the original cubic topology. In this connection, pores are classified according to their size as ultramicropores (<5 Å), micropores (5-20 Å), mesopores (20-500 Å) or macropores (>500 Å). Therefore, several members of this series have pore sizes in the mesoporous range. For example, one member (IRMOF-6) exhibited a high capacity for methane storage and others (IRMOF-8, -10, -12, -14, -15, and -16) the lowest densities, known to date for a crystalline material at room temperature.

This work was used to demonstrate that pore size and functionality could be varied systematically, providing a large number of topologically identical architectures, but with distinctive functionalities.

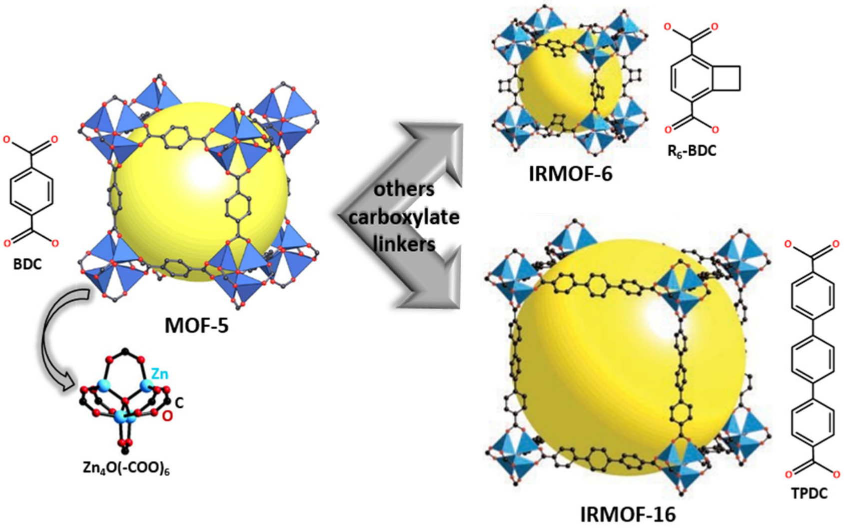


Figure I.10. Single crystal X-ray structure of MOF-5 and IRMOF-n (n = 6 and 16). The large yellow spheres represent the largest van der Waals spheres that would fit in the cavities without touching the frameworks.[89]

The synthesis of MOF-2, MOF-5 and its isoreticular frameworks derivatives proved the successful design of rigid frameworks based on SBUs and therefore the use of reticular chemistry,[80,89] which describes the approach to the synthesis of materials with predesigned building blocks, extended structures, and properties.

Another MOF of great popularity, synthesized the same year, is the HKUST-1, of formula $Cu_3(BTC)_2(H_2O)_3$ (BTC^{3-} = benzene-1,3,5-tricarboxylate).[90] This structure is composed of a $Cu_2(\text{-COO})_4$ secondary building unit, similar to MOF-2. Several isoreticular structures have been made with different linkers, for example, $TATB^{3-}$ (4,4′,4′′-*s*-triazine-2,4,6-triyl-tribenzoate)[91] or BBC^{3-} [4,4′,4′′-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate].[92] In fact, $Cu_3(BBC)_2$ (known as MOF-399) displays a cell volume 17.4 times than of HKUST-1 (**Figure I.11**).

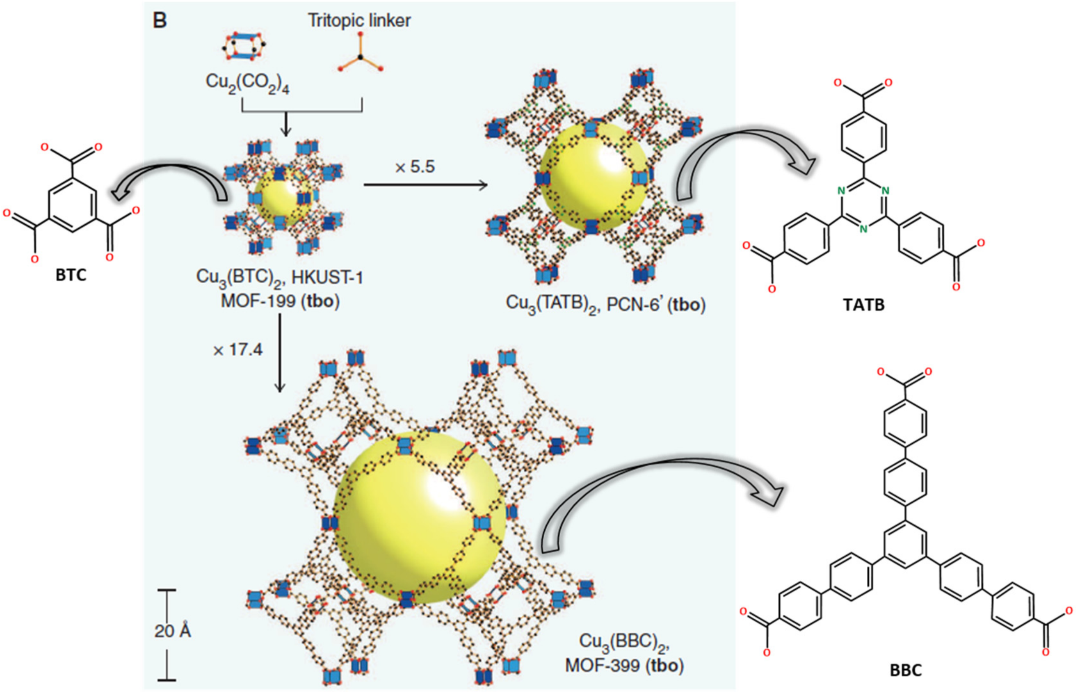


Figure I.11. Isoreticular expansion of HKUST-1. Adapted from ref. 3.

Porous coordination polymers (PCPs) or MOFs, which are microporous materials, could afford not only robust (2nd generation) –with excellent gas storage and separation applications–[64] but also flexible and dynamic (3rd generation) compounds.[65,93] In this connection, flexible MOFs, have received special attention because they provide unique properties related to guest adsorption, different to those of zeolites or rigid porous materials. The flexibility of the porous frameworks is acquired in cooperation with weak bonds, such as hydrogen bonds, π-π stacking or van der Waals interactions, which allow reversible structural transformation of frameworks.

The 3rd generation compounds can alter their frameworks in response to guest molecules, in such a way that they reversibly change their channel structures to accommodate them. They can cause reversible transformations such as rotation of bridging ligands,[94] shrinkage or expansion of the framework depending on guest molecules[87,95,96] or interdigitation and interpenetration of the framework.[97,98] The guest-induced distortion phenomena was classified into three types by S. Kitagawa (**Figure I.12**).[65,99]

- Type I (guest induced crystal-to-amorphous transformation): the network collapse and become amorphous after the removal of guest molecules.[100,101]

- Type II (guest induced crystal-to-crystal transformation): the structural changes in the network are induced by the simultaneous exchange of guest molecules with the retention of crystallinity, which is different from the initial.[102,103]

- Type III (guest induced crystal-to-crystal reformation): the removal of guest molecules transforms the network into a different one.[87,104,105]

In all three cases, the transformations are reversible, so the network reverts to the original one under the initial conditions.

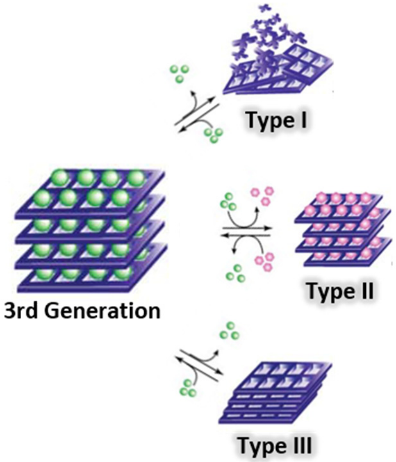


Figure I.12. Classification of dynamic porous coordination polymers by S. Kitagawa. Adapted from ref. 65.

The adsorption of guest molecules in the solid surfaces is not only important for determining the properties of porous compounds but also allows the study of the confined molecules.[106] These molecules and atoms can exhibit interesting properties, which are not observed or are different in the corresponding bulk state, just by being constrained in nanospaces. For this purpose, the interaction between guest molecules and the surfaces is crucial, as well as the control of the pore size and shape.

In the late 1990s, Férey and co-workers introduced the compounds MIL-n (for Materials of Institut Lavoisier),[1] based on trivalent cations and carboxylic acids. One of the most studied MOFs in this family is MIL-53 (**Figure I.13**), which is made up from chromium(III) octahedra and 1,4-benzenedicarboxylic acid ligands.[87] This MOF was one of the first examples of the third generation compounds. MIL-53 exhibited a reversible, shrinkingexpanding framework depending on guest molecules, together with original features such as magnetic properties, high thermal stability, and sorption capacities.[95,96,107,108]

In 2006, Yaghi's group published a new family of MOFs called ZIFs (zeolitic imidazolate frameworks), which presented zeolitic topologies through the use of imidazolates as organic ligands.[109] ZIF-8 (**Figure I.13**), $Zn(MeIM)_2$ ($MeIM^-$ = 2-methylimidazolate), demonstrated permanent porosity, high thermal stability (up to 550 °C), and remarkable chemical resistance. It was the first example of a MOF with exceptional chemical stability, since it remains stable after immersion in boiling methanol, benzene, and water for up to 7 days, and in 0.1 and 8 M aqueous sodium hydroxide at 100 °C for 24 hours.

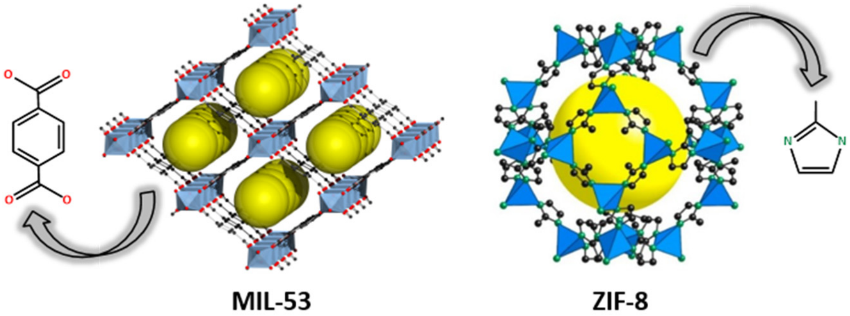


Figure I.13. View of structure of MIL-53 and ZIF-8.

I.3.2. Advantages and Disadvantages of MOFs

Since the porous properties and ways to design MOFs were discovered, they have attracted wide attention by the scientific and industrial communities as new porous materials. This is due to certain advantages they can have over other conventional microporous materials (*e.g.*, zeolites and active carbons) such as:

- Unlike other porous materials, they can be constructed with only an appropriate solvent and without the need to use templating agents.
- The great variety of cations and organic linkers, which can participate in the framework.
- The rational design capability, which allows obtaining of a great diversity of structures with different compositions, topologies and chemical and physical properties.
- The high porosity, high surface area and low densities that they can exhibit, which are very attractive properties for gas storage.
- The robustness or flexibility of their crystalline networks. As already indicated, some of them can show dynamic behaviors in responses to guest molecules.
- The rich host-guest chemistry that they can show.
- The possibility to use single-crystal X-ray diffraction (SCXRD) as the definitive characterization tool.

The most notable disadvantage of MOFs is their thermal stability, which is lower than zeolites and active carbons due to the degradation of the organic part at temperatures between 300-450℃ (rarely more 500℃) depending on the MOF.

I.3.3. Applications

The enormous interest that has arisen for MOFs is due to the large variety of applications[2,28] in many different fields that they can exhibit. Their high and regular porosity provides exceptional properties suitable for technological applications. Moreover, MOFs may exhibit an extend variety of chemical and physical properties. For example, the properties of the traditional porous solids were mainly focused on the exploration of their adsorption performances for various gases and their catalytic potentiality. In addition, they can combine several properties, which suggests the possibility of creating multifunctional materials.[7]

MOFs have shown promising applications such as ion exchange,[110,111] gas storage and separation processes,[26,27] drug transport and delivery,[112,113] for sensor technology,[10,114] catalysis,[31,33,115] hosts for nanoparticles,[39,40] luminescence,[34,35] non-linear optics,[116] magnetism,[11] ferroelectricity,[29,117] among others.

Currently, many efforts are based on the incorporation of new properties in these materials which are appealing for energy, environmental (removal of pollutants) and health-related applications.[118]

Finally, it is worth mentioning that some MOFs (HKUST-1, UiO-66, ZIF-8 or MIL-53 (Al), etc.) are already synthesized on an industrial scale by BASF and marketed by Sigma-Aldrich under the name of Basolite®.

I.3.3.1. Gas Storage and Separation

Gas storage and separation based on the porosity of MOFs is one of the most visible and studied application in the field. It was Kitagawa in 1997 who,[64] with the introduction of methane in a coordination polymer, opened the way for the search for materials able to store gases, due to the high porosity,[109,119,120] and large surface areas[121] that they can present.

The key is the possibility to obtain structures with different pore shapes, sizes and chemical environment (functionality), that is, the tunability of pores. The pore spaces can be efficiently used for gas storage while the sizes and functional sites of the pores can be applied for the selective recognition and uptake of small or large molecules.[28] Therefore, it should be noted that the storage and separation performance of a MOF strongly depends on their synthesis as well as the efficiency of activation (guest removal).

In this context, one of the applications of greater interest, is the use of MOFs as intermediaries in the generation of clean energies, which makes these materials play a vital role in many industries.[26,122,123] In this sense, MOFs can participate in controlled capture and release processes of gases such as hydrogen (H_2),[25] methane (CH_4)[124] and carbon dioxide (CO_2)[24,78] or, in gas separation, as for example CO_2 from CH_4 in natural gas, and purification processes. This is important because H_2 and CH_4 can be used as alternative fuels, since there is a large decrease in fossil fuel reserves, and CO_2 sequestration helps to reduce the anthropogenic impact in the greenhouse effect.

MOFs have also represented a promising new class of material to prepare separation membranes, which are widely applied on an industrial scale to the purification or separation of gases.[125] They can be either integrated into a polymer matrix or grown directly as thin films, having tunable properties.

The molecular separations rely on different microscopic mechanisms: thermodynamic, kinetic, conformational or molecular sieving.[27] When the separation of two or more components is produced by a difference in affinity of adsorbate/MOF, it is considered thermodynamic. This is the most found mechanism in the literature, which has been observed for carbon capture of mixtures of CO_2/CH_4 and CO_2/N_2,[126] and separation of C_2H_2/CO_2, C_2H_2/C_2H_4,[127] etc. It is defined as kinetic separation when it is due to differences in the diffusivity of the adsorbate molecules, that is, the ability/difficulty of molecules to move along the channels of the materials. This mechanism is generally found for molecules that display similar size and functionality such as hydrocarbons.[128] When the separation is owing to steric effects, that is, the pore size/shape allows more efficient packing in a pore, is called conformational. There are a few examples of this in separation of olefins, paraffines or alkanes.[129] Lastly, it is considered a molecular sieving or exclusion-based process, when pore aperture size/shape permits a full-size exclusion of one component from others, allowing infinite selectivity. Very few examples of this mechanism have been published.

The MOFs applications are not limited to gas phase separations so they can be used in the separation of pollutants in liquid phase, including aqueous media.[130] They are successfully employed to capture toxic industrial chemicals like NH_3[131] and H_2S[132] and volatile organic compounds[133] like benzene and xylenes, as well as for the removal of environmentally hazardous gases such as NO_x, SO_x, CO and CO_2,[134] which have harmful effects on the environment. They have also shown the ability to capture chemical warfare agents.[118]

An example of MOF with great potential to capture harmful gases, specifically CO_2, SO_2,[134] as well as NO_2,[135] is NOTT-300, also known as MFM-300(Al). In **Figure I.14**, different gas sorption isotherms can be observed, showing a high affinity for SO_2 and NO_2, with a remarkable high NO_2 uptake.

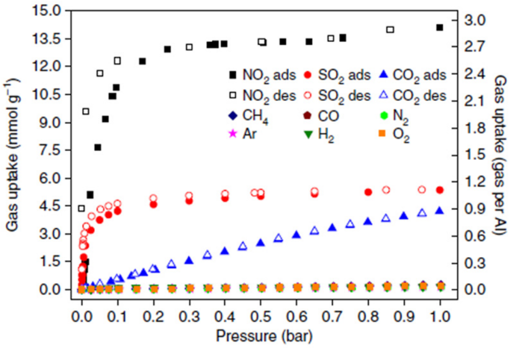


Figure I.14. Comparison of the gas adsorption isotherms for NOTT-300 at 298 K and 1.0 bar. Adapted from ref. 135.

I.3.3.2. Drug Delivery and Biomedicine

MOFs represent a very promising platform for drug delivery due to their high and regular porosity, organic groups within their networks, hydrophilic-hydrophobic cavities and tunable host-guest properties, which make possible to achieve high drug loading as well as its controlled release.[112,136] In addition, they have well-defined crystalline structures that can be characterized by SCXRD, and therefore, this allows a better structural control of the drug insertion and release. The drug carriers are important, owing to they allow a controlled release of the drug and they can solve problems that some therapeutic molecules present, such as instability in biological media and low solubility, among others.

The use of MOFs in this field was first reported by Horcajada and Férey, who demonstrated the loading of an analgesic and anti-inflammatory drug (ibuprofen) into two mesoporous MOFs of MILs family, in particular into MIL-100 and MIL-101, which exhibited remarkable ibuprofen uptake and the release of the drug at physiological pH.[113,137] Also, MOFs of MIL series can absorb anti-tumor and anti-AIDS (Acquired Immune Deficiency Syndrome) active agents.[138]

This work triggered many other studies focused on the use of MOFs for biomedical applications,[36,37] for which it is required that these compounds have a biologically friendly composition. For that purpose, it is important to choose toxicologically acceptable MOFs. In principle, most metals and linkers could be used but at doses below their degree of toxicity. However, it should also be considered the daily requirements of the human body to select the metal, for example calcium, magnesium, and to a lesser extent, zinc and iron would be appropriate metals. Regarding the linker, there are two possibilities, exogenous or endogenous linkers. The difference is that the former do not intervene in the body cycles, nevertheless it has been the most common so far. Another factor to keep in mind is the biodegradability of the material, since it is important that they are sufficiently stable to achieve their function and then to be removed or recycled by the body to prevent their accumulation. Also, it is relevant the possibility to make suitable devices for the practical application of the material, with respect to this, the MOFs have been able to prepare as pellets, films, stable solutions of nanoparticles, etc.

Another biomedical application of these compounds have focused on their use as delivery vehicles for imaging contrast, which requires the use of nanoscale metal-organic frameworks (NMOFs). It has been demonstrated the potential of MOFs based on paramagnetic metals as contrast agents for magnetic resonance (MR) imaging, for which the strategy of incorporating nanoparticles in the MOFs has been used.[139] The first study was carried out with Gd-based MOFs by Lin and co-workers.[140] Given the toxicity of Gd^{3+} that prevents its clinical application, they worked to obtain other compounds with lower toxicity such as Fe/Mn-based MOFs.[141,142]

I.3.3.3. Catalysis

The catalytic applications of MOFs[31,33,115] have emerged as an important research field and were one of the earliest proposed[59] and demonstrated[19] applications. The advantage of MOFs is that they offer multiple opportunities to create one or more active catalytic sites within the pores. A wide variety of metallic centers can be used for their synthesis and it is possible to create different environments depending on the ligand used and its functionalization. MOFs have a great design flexibility, which differentiates them from traditional materials such as zeolites. Moreover, MOFs have high porosity with tunable channels/cavities at the nanoscale level, while zeolites have a more limited pore size but their chemical and thermal stability is greater.

MOFs have become promising candidates for heterogeneous catalysis in industrial applications, because they can be maintained during the catalytic processes, and thus they can be recycled and reused for several times, showing economic and environmental advantages for industries, unlike the homogeneous catalysts.

There are different strategies to synthesize catalytically active MOFs, in which both the metal centers and the ligands can act as catalytic centers.[33,115] The metal ions in MOFs structures play an essential role as node points, therefore, in most cases they are not available for catalysis. However, it is possible to generate open metal sites in the framework by removing guest solvent molecules coordinated to these metal centres without destruction of the structures, getting unsaturated coordination environments, which can be utilized as active catalyst sites. This strategy was first adopted for the MOF-11, with the formula $Cu_2(ATC)\cdot 6H_2O$ (ATC^{4-} = 1,3,5,7-adamantanetetracarboxylate), which have two water molecules acting as a ligand and four molecules acting as guests.[143] All guest molecules, including the coordinated water molecules, could be eliminated to provide a stable structure with exposed copper sites. Many MOFs have been obtained with open metal sites –such as HKUST-1,[144,145] MIL-100,[146] MIL-101[147,148] and UiO-66[149]– and they can be used as mild Lewis acids or in the oxidation of organic substrates. For example, the free Cr^{III} coordination sites in the MIL-101 catalyze the cyanosilylation of aldehydes (**Figure I.15**).[147]

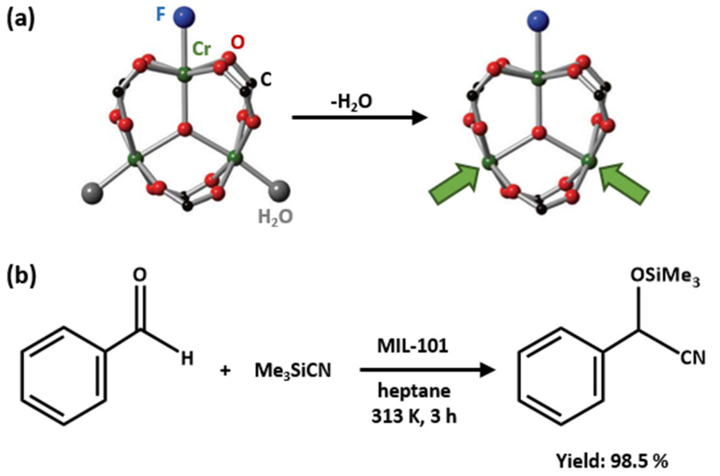


Figure I.15. (a) Open metal sites (green arrows) in trimeric chromium(III)-SBU of MIL-101(Cr) and (b) reaction of benzaldehyde cyanosilylation catalyzed by MIL-101.

In addition, these unsaturated metal centres can be used as anchoring points for additional functional groups because of their electron deficiency. For example, using post-synthetic procedures, the coordinatively unsaturated chromium(III) sites in MIL-101(Cr) were functionalized with ethylenediamine. The free amine group performed the function of immobilizing palladium nanoparticles to be applied in coupling reaction.[150]

The bridging ligands of the MOF can also contain catalytically active functional groups,[31] which can act as either Lewis acids or bases or be designed for the anchoring of metal active centers. There is a wide variety of organic functional groups that can serve as active sites such as alcohols, amides, amines, carboxylates and pyridines. An example of this was reported in the MOF obtained by Kitagawa's group, in which the presence of accessible amides in the network allows to catalyze the Knoevenagel condensation reaction.[151] It is also possible to use chiral organic ligands to design MOFs containing chiral centers with catalytic capacity for asymmetric catalysis.[152]

On the other hand, MOFs can also present catalytic activity by incorporating active guest species in their pores, such as complexes or inorganic nanoparticles or serving as templates for the preparation of nanoclusters (NCs) and nanoparticles (NPs) through the use of post-synthetic methods (PSMs).[39] For example, the immobilization of a cationic metalloporphyrin complex inside the anionic framework of a MOF, during the synthesis, allowed to catalyze the oxidation of cyclohexane.[153]

I.3.3.4. Sensing and Luminescence

A chemical sensor is a self-contained analytical device that can give information about the chemical composition of its environment (in liquid or gas phase). It is designed to absorb or react selectively with analytes, which can be monitored through the changes that occur in the electrical, photophysical or mechanical properties of the device.[10] Therefore, they are very useful for a wide range of applications such as environmental monitoring, occupational safety, medical diagnostics, chemical threat detection, quality controlling or industrial process management.

Since MOFs have intrinsic permanent porosity, structural flexibility and tunable capacity (pore's size, shape, chemical composition), they can be designed for the selective capture of certain molecules (volatile organic compounds, gases, ionic species, biomolecules, explosives, etc.), which makes them very promising as chemical sensors.[154,155] Moreover, their porous nature allows to adsorb and pre-concentrate the analytes at the sensor, which increases the possibility of host-guest interactions and improve sensing performance. MOF-based sensors can be selective, sensitive, stable, reusable, as well as having adequate response times, meeting the expectations required to be used as sensors. It should be noted that there are two types of sensors based on MOFs. On the one hand, those in which their own structure and properties respond to an external stimulation, and on the other hand, those whose response depends on the guest, exhibiting optical, magnetic or electronic properties based on the guest-host interactions.

The most studied types of MOF sensors so far are based on photoluminescence. The main advantage that makes luminescence more popular than other transduction mechanisms is the production of a quick and easy colorimetric response to stimuli, so the signal can be recognized easily either by eyes or by fluorescence spectrometers.[10,35]

The luminescence is the emission of light stimulated by the absorption of energy and generally takes place by two mechanisms: fluorescence, which is the most common, and phosphorescence (**Figure I.16**). In the first case, the emission is based on spin-allowed transition from the singlet excited state S_1 to the singlet ground state S_0 and in the second case, there is a spin-forbidden intersystem crossing from the singlet excited state S_1 to the triplet excited state T_1 (lower energy state than S_1), followed by a transition to ground state S_0, with lifetimes that can be as long as several seconds.[34]

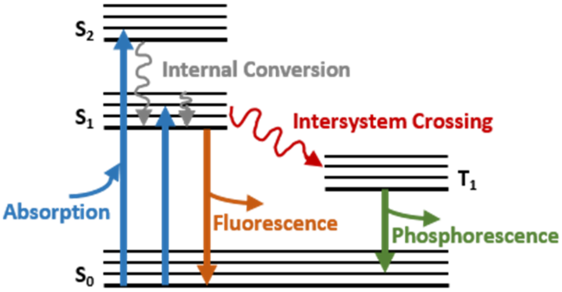


Figure I.16. Jablonski diagram.

In MOFs, the luminescence can arise from their organic linkers, metal ions or guest molecules (**Figure I.17**).[34] One of the most common types is ligand-centered luminescence (generally in aromatic or conjugated organic compounds), including ligand-localized emission as well as ligand-to-ligand charge transfer (LLCT), ligand-to-metal charge transfer

(LMCT) and metal-to-ligand charge transfer (MLCT). The LMCT and MLCT effects are common in MOFs with d^{10} transition metals. Whereas LMCT processes have been observed in MOFs based on Zn(II)[156] and Cd(II),[157] MLCT effects are present in MOFs based on Cu(I)[158,159] and Ag(I).[159,160] On the other hand, metal-centered luminescence is seen in MOFs containing rare earth elements as the lanthanide trivalent ions.[161] In some cases, several of these effects may occur and compete.[157]

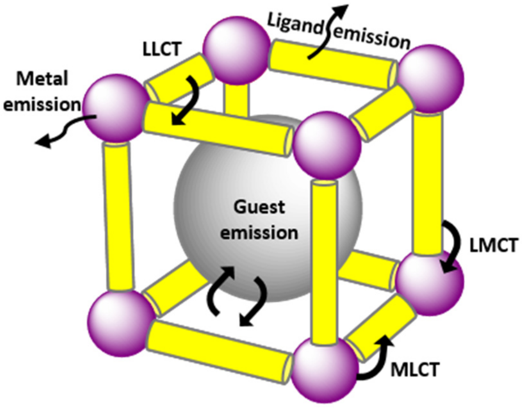


Figure I.17. Representation of emission possibilities in a porous MOF. Inorganic SBUs, purple spheres; organic linkers, yellow cylinders; guest chromophores, gray sphere inside.

The fact that the organic ligands are part of the network and therefore, their mobility is restricted, as well as the conjugated groups have ordered orientation, makes it possible to reduce the nonradioactive relaxation caused by the free rotation and vibration of the ligand, improving the quantum efficiency of the system.[162] Concerning the guest molecules, which can be emitters or sensitizers, they can alter the emission properties of the host, inducing changes that can be detected in emission profiles, such as displacements of its wavelength, changes in intensity or a completely different emission.[163] Therefore, the encapsulation of guest molecules can provide luminescent properties to a non-luminescent MOF or even lead to the formation of new species with different properties through the MOF-guest interactions.[164,165] This makes possible to modulate the luminescence of the MOF by incorporating specific molecules, and as a result its use as a sensor.

Luminescent metal-organic frameworks (LMOFs) based sensors have been used to detect a large number of stimuli such as ions,[166] volatile organic compounds (VOCs),[167] explosives,[168] biomolecules,[169] toxic species,[170] gas,[171] humidity,[172] temperature[173] or pH,[174] thus demonstrating its efficiency and versatility.

I.3.3.5. Magnetism

The possibility of incorporating two properties into a material, *i.e.*, porosity and magnetism, has generated great interest, since this makes possible to obtain multifunctional magnetic materials and use them as magnetic sensors, molecular magnets or to carry out magnetic separations.[11,175,176]

Magnetic properties can be introduced into MOFs, selecting the appropriate organic linkers and the inorganic sub-units (metal centers, clusters, etc.), as well as controlling the way they are linked in the solid or even by the insertion of guest molecules into the cavities.[177,178]

Magnetic MOFs can exhibit cooperative magnetic properties (magnetic ordering or cooperative spin crossover) and molecular magnetic properties (single-ion magnet behavior, where the molecules are isolated by organic spacers) depending on the dimensionality of the inorganic nodes and the extended framework.[11] The word "cooperative" refers to the interaction (coupling) between the spins of neighboring paramagnetic metal centers through organic linkers within the infinite ordered network. This interaction leads to the ordering of the spins below a characteristic temperature, known as a critical temperature (T_c). This T is achieved by measuring the magnetization of the material when applying an external magnetic field at a variable temperature (**Figure I.18**). Different magnetic phenomena can be observed as antiferromagnetism, ferrimagnetism and ferromagnetism, in which an antiparallel, unequal antiparallel or parallel coupling of spins is produced, respectively (**Figure I.19**). In the magnetic interactions, the sign and the strength depend on both the nature of the magnetic carriers and on geometrical criteria concerning the M-L-M angles.

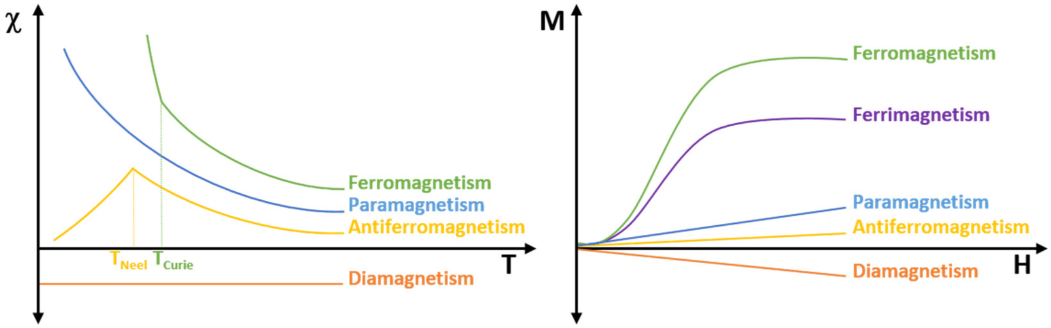


Figure I.18. Curves of susceptibility (χ) vs. temperature (T) and magnetization (M) vs. magnetic field (H).

Figure I.19. Behaviour of the materials for an applied magnetic field.

The linkers are responsible for transmitting the magnetic information between the metal centers to obtain a magnetic MOF with cooperative properties. To this end, short distances between paramagnetic centers are preferable. However, porosity is often favored with the use of long linkers. Thus, to combine both properties, diverse synthetic strategies have been used in literature, such as use of short linkers (formates,[179] cyanides,[180] azolates,[181] diazines,[182] and lactates[183]), metalloligands[9,175] or radical ligands.[101]

In our group, oxamato- and oxamidato-based metalloligands are usually employed[184] and they are a convenient approach (so-called "complex-as-ligand") for obtaining magnetic MOFs with high T_c. They are transition metal complexes that possess vacant coordination sites that can act as a building block. Such complexes are joined by additional metal ions to prepare metal-organic frameworks. Using this strategy, an anionic MOF, of formula $[Na(H_2O)_{3.25}]_4\{Mn_4[Cu_2(Me_3mpba)_2(H_2O)_{3.33}]_3\}\cdot 37H_2O$ [Me_3mpba^{4-} = *N,N'*-2,4,6-trimethyl-1,3-phenylenebis(oxamato)], with a ferromagnetic ordering dependent on the guest molecules was obtained (**Figure I.20**).[175] The compound is formed by oxamato-based dinuclear Cu^{II}_2 metallacyclic complexes that have free carbonyl-oxygen atoms, whereby Mn^{II} ions coordinate creating a 3D network.

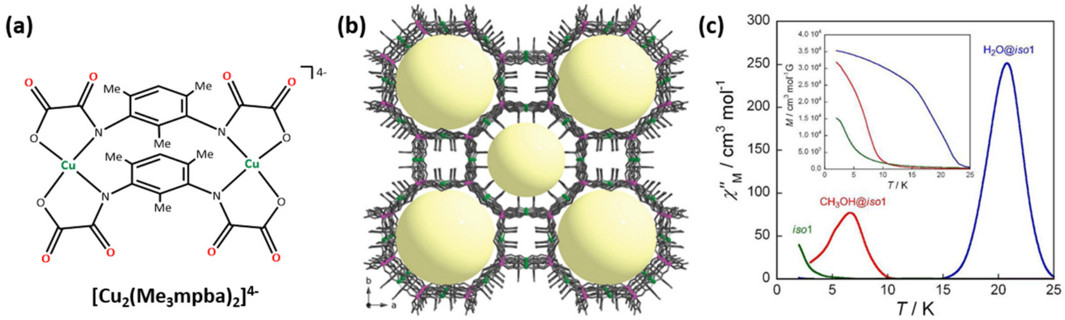


Figure I.20. (a) Scheme of the metalloligand $Na_4[Cu_2(Me_3mpba)_2]\cdot 4H_2O$; (b) projection view of $[Na(H_2O)_{3.25}]_4\{Mn_4[Cu_2(Me_3mpba)_2(H_2O)_{3.33}]_3\}\cdot 37H_2O$; (c) temperature dependence of the ac out-of-phase molar magnetic susceptibility (χ''_M) of MOF with different guest molecules. Adapted from ref. 175.

Another phenomenon that usually occurs in MOFs, and does not require a magnetic interaction between neighboring metal centers, is the spin crossover (SCO). This phenomenon is based on the change in the electronic configuration of a transition metal ion between high spin and low spin states, in response to external stimuli (magnetic field, electrical field, temperature, pressure, guests incorporation).[185] Although it is not produced by a magnetic exchange between the spin-crossover centers, the cooperative effects between them are necessary. In these cases, the length of the ligand is not determinant, however, the ligand field and the coordination environment must be appropriate. In addition, the spin crossover behavior is affected by guest molecules (gases, solvents, halogens, and organic molecules) through host-guest interactions, which has been studied in several publications.[186,187] For example, this effect has been observed in the family of Hofmann-type iron(II), in particular $[Fe^{II}(pz)M^{II}(CN)_4]\cdot G$ (pz = pyrazine; M = Pt or Ni, G = guest), where the SCO phenomena and porosity coexist (**Figure I.21**).[176,188]

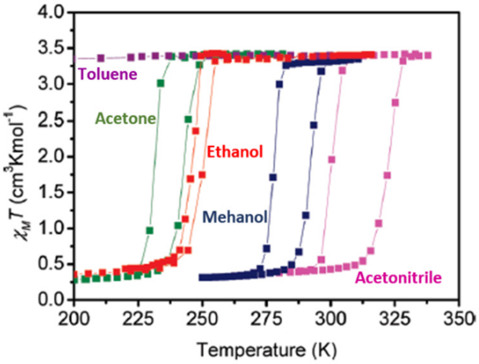


Figure I.21. Spin transition behavior of [Fe^{II}(pz)Ni^{II}(CN)$_4$]·G, where G is toluene (purple), acetone (green), ethanol (red), methanol (blue) or acetonitrile (pink).[188]

Also, it is possible that the magnetic behavior of MOFs is due to the presence of single-molecule magnets (SMMs) in the inorganic nodes, producing a slow relaxation of the magnetization at low temperatures. The SMMs are usually constructed by polynuclear clusters[189,190] or lately, by mononuclear metal complexes (known as single-ion magnets, SIMs),[191,192] with a high magnetic anisotropy. Single-ion magnets have the advantage that they can combine huge magnetic anisotropies with strong quantum effects. They are usually based on lanthanides[190,191] or transition metals.[192]

One of the first examples of SIM-MOF was the compound of formula [Co(bpeb)$_2$(NCS)$_2$]·nG [bpeb = 1,4-bis(pyridine-4-ylethynyl)benzene, G = guest] reported by J. Vallejo.[192] This 2D MOF (**Figure I.22**) is formed by octahedral cobalt(II) SIMs and has cavities that are occupied with aromatic guest molecules that can be exchanged, showing slow magnetic relaxation effects dependent on the guest molecule.

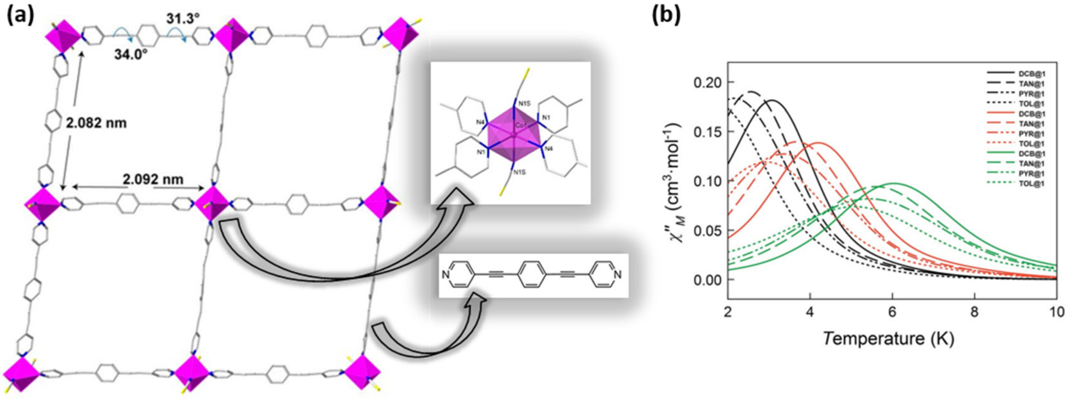


Figure I.22. (a) Perspective view of a fragment of the neutral square grid-type flat layers of [Co(bpeb)$_2$(NCS)$_2$]·7DCB (DCB@1); (b) temperature dependence of χ''$_M$ of [Co(bpeb)$_2$(NCS)$_2$]·nG with different guest molecules (G). Adapted from ref. 192.

I.4. Oxamato/Oxamidato-based MOFs

There are numerous synthetic routes to prepare MOFs. In this thesis, as said before, we have focused on the use of the "complex-as-ligand" approach, with oxamate or oxamidate ligands derived from amino acids. In this strategy, transition metal complexes act as metalloligands toward transition or alkaline earth metals ions to assemble the MOFs. The use of this strategy is one way to gain control over the dimensionality and topology of the networks, favoring the combination of different physical properties in a given material.

Our group has extensive experience in coordination chemistry, specially in the oxamate and oxamidate chemistry to obtain magnetic coordination polymers.[9] Thus, this expertise has been used to design new multifunctional high-dimensional MOFs with tunable pores that can present other types of physical and chemical properties or can act as chemical reactors to construct novel species, making them useful for various applications such as catalysis, gas adsorption, water remediation, among others.

I.4.1. Advantages Oxamato and Oxamidato Metalloligands

The oxamate and oxamidate dianions (Figure I.23a) can adopt bidentate and bis(bidentate) coordination modes in the metal complexes, to produce mono- or polinuclear[184,193] compounds in *cis* or *trans* conformation[194] (Figure I.23b).

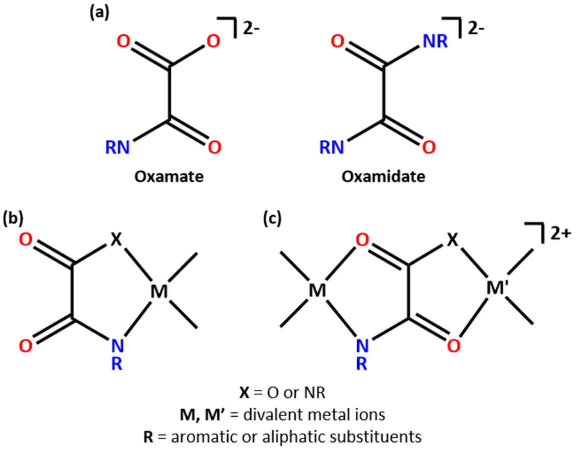


Figure I.23. (a) Oxamate and oxamidate dianions; (b) mono- and (c) dinuclear complexes.

Complexes (mono-, di-, or trinuclear) formed from these ligands have a high stability in solution.[194] This is due to the strong electron-donating capacity of the *N,O*-oxamate and *N,N*-oxamidate groups, which show an excellent coordination affinity towards the divalent metal ions of the first transition series (Cu^{II}, Ni^{II} and Co^{II}). Besides, the fact that these complexes have free carbonyl-oxygen atoms make them capable of binding other divalent transition or alkaline earth metal ions (Ni^{II}, Co^{II} and Mn^{II}) offering the possibility of forming heterobimetallic CPs,[184,193] where the complexes act as stable and robust building blocks.

Concerning the magnetic properties, the bis(bidentate) oxamate and oxamidate bridges mediate magnetic interactions between the neighbouring paramagnetic metal ions, allowing long-range magnetic ordering,[195] single-molecule magnet (SMM)[196] or single-chain magnet (SCM)[197] behaviours. It should be noted that oxamide/oxamidate bridges allow stronger magnetic interactions between metal centers than oxalates ones, due to the lower electronegativity of the nitrogen atoms compared to the oxygen ones.

The oxamato-based MOFs can present anionic and porous framework structures,[175,198] which offer the opportunity to introduce different countercations in the channels,[178] providing additional physical properties to the material, and thus, makes them appropriate candidates to obtain multifunctional materials.

Another advantage of this type of ligands is that they are easily functionalized and prepared, simply by reacting oxalyl chloride, ethyl oxalyl chloride or diethyl oxalate with the appropriate amine precursor.[194] This makes easier the incorporation of the desired properties (*e.g.*, luminescence, chirality, magnetism, among others) into a material.[199,200]

The amino acids are organic compounds formed by a carboxyl (-COOH) and an amine (-NH_2) functional groups, as well as a specific side chain (R group) (**Figure I.24**), which provides each amino acid with its set of properties (charged, polar, aromatic, aliphatic, etc.). The presence of the amino group makes them fantastic precursors to form oxamate or oxamidate ligands,[199,201] offering remarkable advantages to the final structure such as biocompatibility, stability in water, rich structural diversity, chirality, as well as specific properties depending on the side chain.

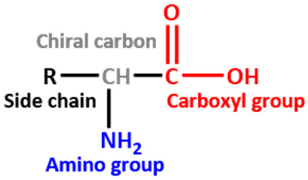


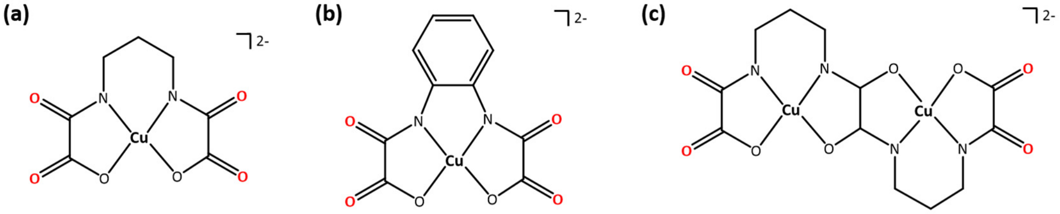
Figure I.24. Amino acid structure.

I.4.2. Previous Results

In 1986, the group led by O. Kahn began using mononuclear and dinuclear Cu^{II} complexes derived from oxamate ligands (**Figure I.25a**), with the aim of designing polymetallic systems (chain compounds) that exhibit predictable molecular magnetic properties.[202,203] He decided to use this type of complexes motivated by the work published by Nonoyama and co-workers in the late 1970s,[204] in which they showed that the *N*-monosubstituted oxamide derivatives were very interesting, since they could form several complexes of Cu^{II} and Ni^{II}.

The pioneer work of Kahn's group in the late 1980s[202,203,205,206] and later extended to the oxamidate analogues by Journaux's and Lloret's groups in the late 1990s,[194,207-209] showed the important role of these complexes in the field of magnetism. They used aliphatic or aromatic group-substituted bis(oxamato)- and bis(oxamidato)-copper(II) complexes as metalloligands (**Figure I.25**), toward other metal ions (*e.g.*, Mn^{2+} or Co^{2+}) to obtain molecule based-magnets. Initially, one-dimensional compounds[206,208] were obtained and later, they focused on the preparation of two- or three-dimensional structures in order to move T_c towards higher temperatures.[209-213]

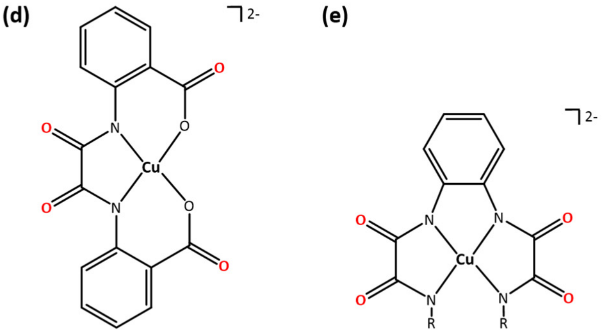
Journaux and Lloret utilized *N,N'*-bis(substituted)oxamides to improve its solubility, since oxamide is insoluble in common solvents, as well as trying to avoid the hydrolytic reaction that undergoes under deprotonation, producing oxalate.[194,209]



$[Cu(pba)]^{2-}$
pba = *N,N'*-1,3-propylenebis(oxamato)

$[Cu(opba)]^{2-}$
opba = *N,N'*-1,2-phenylenebis(oxamato)

$[Cu_2(bapo)]^{2-}$
bapo = *N,N'*-bis(oxamato-1,3-propylene)oxamido



$[Cu(obbz)]^{2-}$
obbz = *N,N'*-oxamidobis(2-benzoato)

$[Cu(R_2opbox)]^{2-}$
opbox = *N,N'*-1,2-phenylenebis(oxamido)
R = aromatic or aliphatic substituents

Figure I.25. Some oxamato and oxamidato copper(II) complexes used by the groups of Kahn, Journaux and Lloret. (a) $[Cu(pba)]^{2-}$,[202,203,205,206] (b) $[Cu(opba)]^{2-}$,[210-213] (c) $[Cu_2(bapo)]^{2-}$,[202] (d) $[Cu(obbz)]^{2-}$,[207,208] and (e) $[Cu(R_2opbox)]^{2-}$.[209] The red atoms represent the free coordination sites.

Our group, taking advantage of the benefits provided by the use of oxamato/oxamidato-bridged polymetallic complexes (**Figure I.26**) acting as metalloligands, has obtained a wide variety of nD magnetic materials (discrete polynuclear coordination compounds or infinite multidimensional coordination polymers) as well as multifunctional materials.[9]

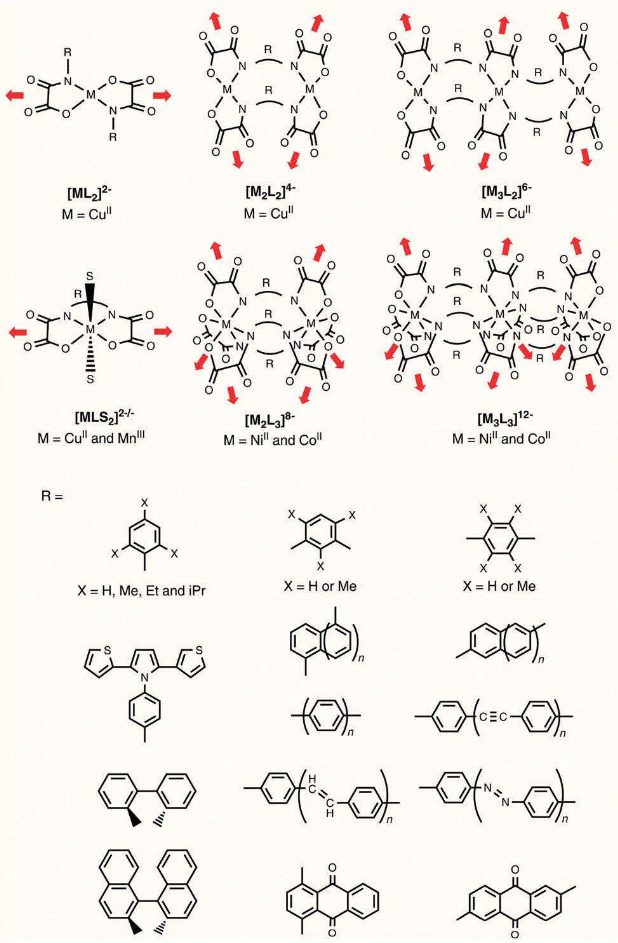
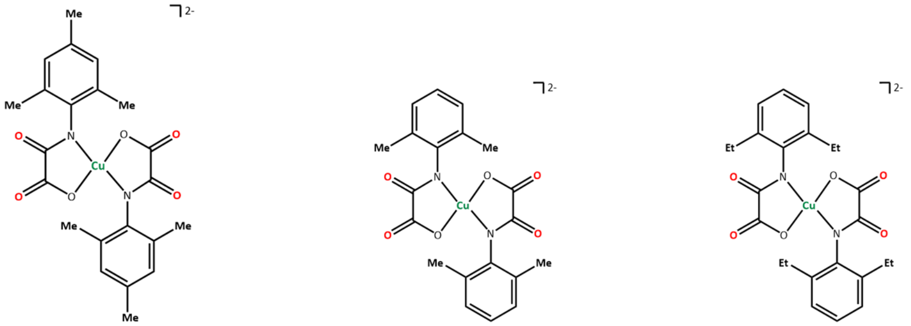
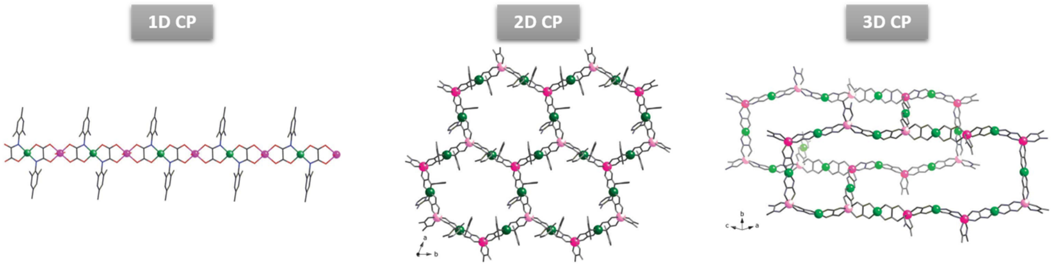


Figure I.26. Oligonuclear aromatic oxamato complexes used as metalloligands (S = labile solvent molecules). The red arrows represent the free coordination sites. Adapted from ref. 9.

In this context, a wide variety of *N*-substituted aromatic oligo(oxamate) ligands have been used to obtain mono-, di- and trinuclear complexes,[9,184] as illustrated in the **Figure I.26**. For example, using dianionic oxamato-containing mononuclear copper(II) complexes, $[CuL_2]^{2-}$, as bis(bidentate) metalloligands, heterobimetallic chains with single-chain magnet (SCM) behaviour were built (**Figure I.27**).[197,214] In addition, the influence of the length of the alkyl-substituents present in the aromatic ring of the oxamate ligands in these mononuclear complexes and the use of different divalent ions were studied, which made it possible to obtain high dimensionality compounds (2D and 3D CPs) with long-range magnetic ordering (**Figure I.27**)[195] In the case of anionic dinuclear copper(II) complexes, $[Cu_2L_2]^{4-}$, with π-conjugated phenylene spacers, as tetrakis(bidentate) metalloligands towards M^{2+} ions, also yielded 1D, 2D[215-217] or 3D CPs,[175,218] with magnetic properties (**Figure I.28**). CPs were not only obtained with copper complexes, but also with nickel and cobalt. In particular, the dinickel(II) and dicobalt(II) complexes, $[M_2L_3]^{8-}$, showed that can act as hexakis(bidentate) metalloligand –instead of tetrakis(bidentate) ligand as the case of Cu(II)– for the construction of 3D frameworks.[219,220]



$[Cu(Me_3pma)_2]^{2-}$ $[Cu(Me_2pma)_2]^{2-}$ $[Cu(Et_2pma)_2]^{2-}$

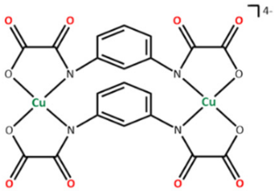


$[CoCu(Me_3pma)_2(H_2O)_2]_n·4nH_2O$
Me_3pma = *N*-2,4,6-trimethylphenyloxamato

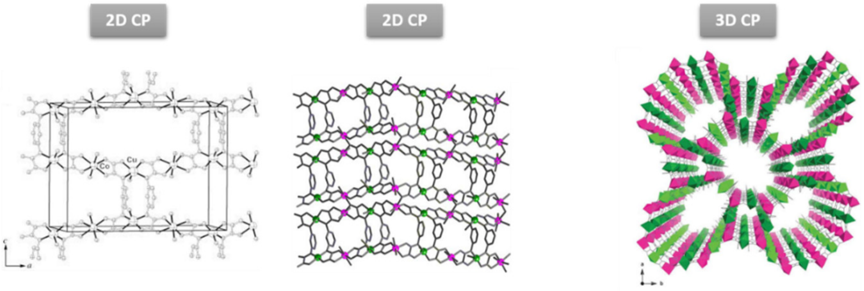
$(n\text{-}Bu_4N)_4[Mn_4Cu_6(Me_2pma)_{12}]·2dmso$
Me_2pma = *N*-2,6-dimethylphenyloxamato
$n\text{-}Bu_4N^+$ = tetra-n-butylammonium cation

$(n\text{-}Bu_4N)_4[Mn_4Cu_6(Et_2pma)_{12}]$
Et_2pma = *N*-2,6-diethylphenyloxamato

Figure I.27. Mononuclear copper(II) complexes (top) and perspective view of 1D,[214] 2D[195] and 3D[195] coordination polymers (bottom) obtained from the respective complexes. Cu and Mn or Co atoms are represented by green and purple spheres, respectively.



$[Cu_2(mpba)_2]^{4-}$
mpba = *N,N'*-1,3-phenylenebis(oxamato)



$[Co_2Cu_2(mpba)_2(H_2O)_6]·6H_2O$ $[Mn_4Cu_4(mpba)_4(H_2O)_9]·14H_2O$ $[Na(H_2O)_4]_4[Mn_4\{Cu_2(mpba)_2(H_2O)_4\}_3]·56.5H_2O$

Figure I.28. Dinuclear copper(II) complex (top) and perspective view of 2D[216,217] and 3D[218] coordination polymers (bottom) obtained from this complex. Cu and Mn atoms are represented by green and purple, respectively.

Later, the efforts of our group focused on the incorporation of other physical property in addition to the magnetic one, such as porosity, luminescence or chirality, with the aim of preparing multifunctional magnetic coordination polymers (MMCPs).

For the purpose of incorporating chirality, different synthetic strategies were employed. It was possible to obtain heterobimetallic chiral single chain magnets (CSCMs) by the reaction of enantiopure mononuclear complexes with divalent metal ions.[221,222] Also, 3D-CPs were prepared by the reaction of dinuclear complexes with divalent metal ions in the presence of chiral cations and oxalate dianions,[223] or by the reaction of mononuclear complexes with chiral countercation towards divalent metal ions.[224]

In order to obtain porous magnets, in which coexist long-range magnetic ordering and porosity, 3D metal-organic frameworks were synthesized using the metalloligand strategy. In particular, the 3D framework that is observed in **Figure I.28** and presents pillared layer structure with mixed square and octagonal pores, showed reversible switching from a crystalline hydrated phase with long-range ferromagnetic ordering to an amorphous dehydrated phase.[218] Unlike this one, a anhydrous isoreticular analogue, of formula $Na_4\{Mn_4[Cu_2(Me_3mpba)_2]_3\}$ [Me_3mpba^{4-} = *N,N′*-2,4,6-trimethyl-1,3-phenylenebis(oxamato)] obtained by the same type of ligand but with methyl substituent in the aromatic ring (**Figure I.20**), exhibited selective gas and vapor sorption behavior, demonstrating the fascinating potential of this class of oxamato-based MOFs.[175]

Another strategy used to introduce or improve the physical properties in a preformed MOF has been the emergent post-synthetic methods, such as metal substitution (transmetallation) or the exchange of guest molecules hosted in the pores.[198,225] In the case of the anionic MOF (**Figure I.29**), $Na_4\{Mn_4[Cu_2(Me_3mpba)_2]_3\}\cdot 60H_2O$, the replacement of the Na^I ions hosted in the channels by Li^I or K^I ions through single-crystal to single-crystal (SC to SC) process, provided an improvement of both the gas adsorption and magnetic properties.[225]

Lately, our research group has prepared new multifunctional materials using oxamate and oxamidate ligands, but in this case, derived from enantiopure amino acids.[199,201,226-228] They offer the possibility of forming chiral materials, due to the presence in their structures of asymmetric α-carbon atoms, as well as exhibit other properties.

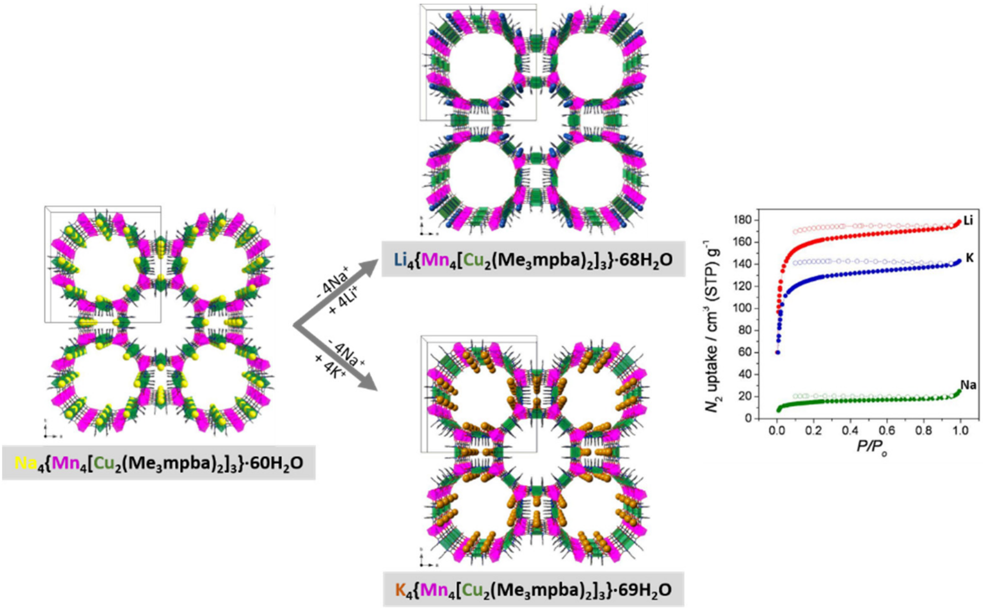


Figure I.29. Perspective view of 3D anionic networks along the crystallographic *c* axes, and low-pressure N_2 (77 K) sorption isotherms. Adapted from ref. 225.

The synthesis of oxamate[228] and disubstituted oxamidate[226] proligands was carried out by the reaction of the methyl ester derivatives of the corresponding enantiopure amino acid with ethyl oxalyl chloride or oxalyl chloride, respectively, as shown in the **Figure I.30**. These proligands offer multiple coordination sites through the carbonyl and the deprotonated amidate and carboxylate donor groups. So, firstly, copper(II) complexes were prepared from them, and then these complexes were used as metalloligands towards transition or alkaline earth metal ions to assemble the targeted MOFs.

In the case of disubstituted oxamidato ligands, dinuclear copper(II) complexes were obtained (**Figure I.31a**), and they acted as bis(tridentate) bridging ligands towards divalent metals ions (Ca^{II} or Ba^{II}) to build chiral MOFs.[201,226,227] In particular, enantiopure derivatives of alanine, leucine and valine were used (**Figure I.31b**), which have hydrophobic aliphatic side chains of different length. This fact, together with that the family of chiral 3D barium(II)−copper(II) networks obtained from the corresponding amino acids showed different architectures, allowed studying the effect of the size of the aliphatic residue of the amino acid on the final 3D structure.[226] Moreover, the isoreticular family of chiral 3D calcium(II)−copper(II) networks exhibited water stability, permanent microporosity, good results in gas adsorption and separation[227] (**Figure I.31c and d**), and even, proton conductivity,[201] proving the amazing possibilities of MOFs derived from enantiopure amino acids.

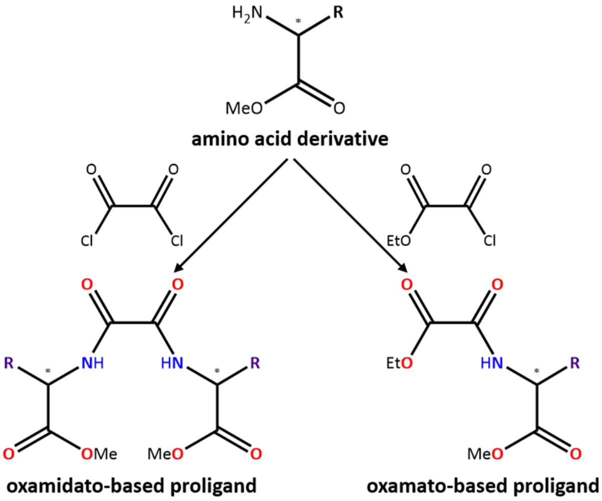


Figure I.30. Synthetic route for the preparation of proligands derived of amino acids, where the R refers to the amino acid residue and (*) indicates the asymmetric α-carbon atom. The red (O) and blue (N) atoms represent the coordination sites.

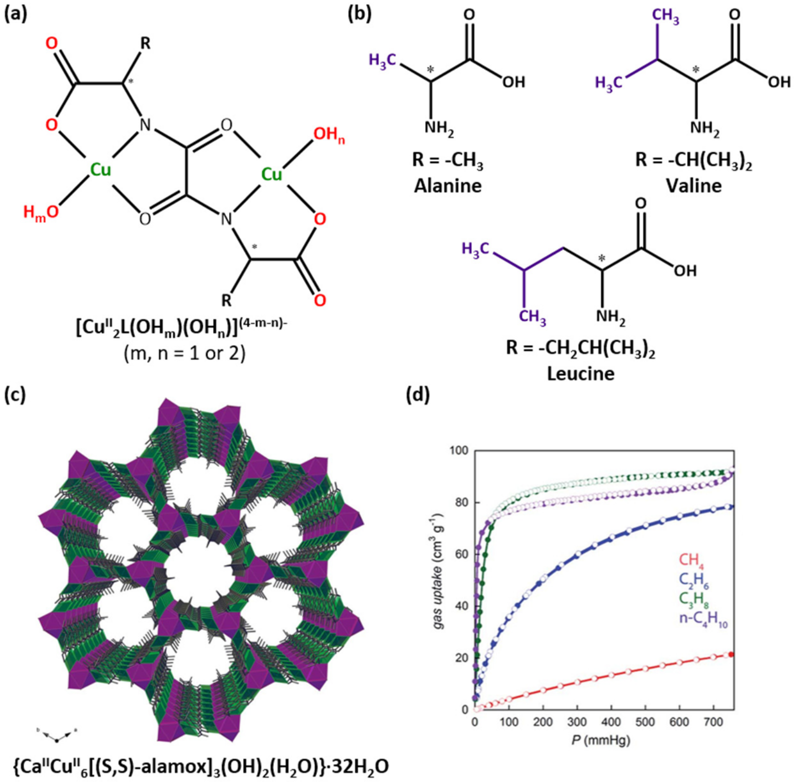


Figure I.31. (a) Dinuclear copper(II) complex obtained from oxamidato-based proligand; (b) amino acids used; (c) perspective view of the 3D structure obtained from *L*-alanine; (d) adsorption isotherms of different hydrocarbons of $\{Ca^{II}Cu^{II}_6[(S,S)\text{-alamox}]_3(OH)_2(H_2O)\}\cdot 32H_2O$ [(*S,S*)-alamox = bis[(*L*)-alanine]oxalyl diamide]. Adapted from ref. 201 and 227.

On the basis of these results and with the aim to obtain new multifunctional materials of potential technological and sustainable applications, in this thesis, we have used different amino acids derivatives, such as *L*-methionine, *L*-serine, *L*-threonine or *L*-histidine methyl ester (**Figure I.32**), in order to obtain oxamidato-based MOFs. For that purpose, the aforementioned strategy has been adopted, consisting of preparing stable dicopper(II) complexes, from the corresponding synthesized oxamidate proligands, which are able to coordinate to other ions (Ca^{II}, Sr^{II}, etc.), acting as metalloligands, to give rise to three-dimensional networks. In the following figure (**Figure I.33**), the general synthetic route used to obtain some of the MOFs reported in this thesis is observed.

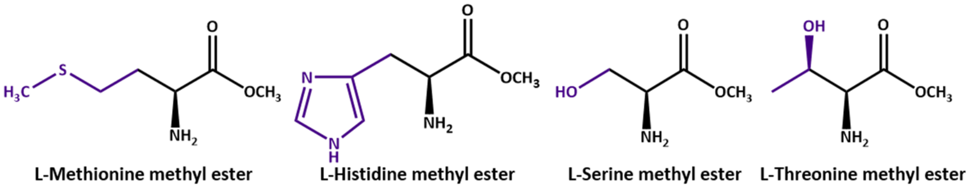


Figure I.32. Derivatives of amino acids used for the studies developed in this thesis.

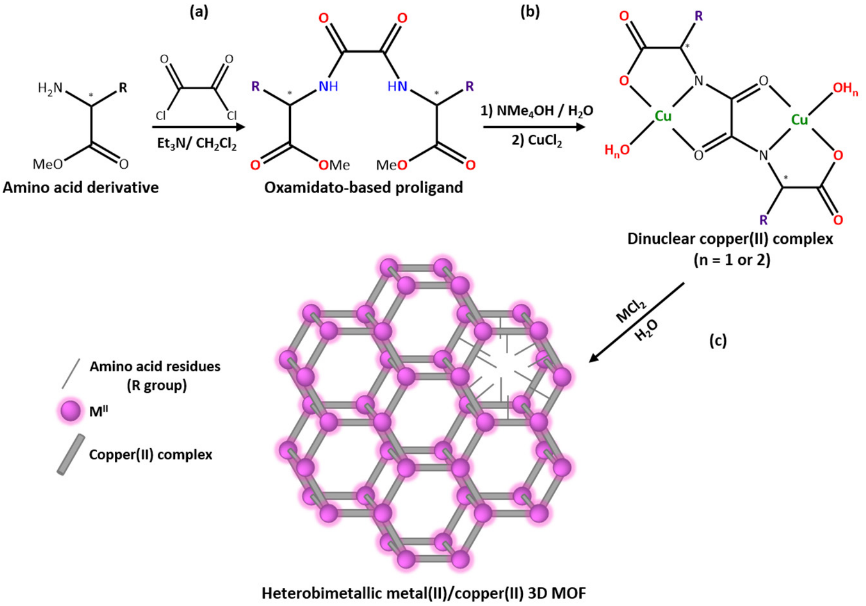


Figure I.33. Scheme of the synthetic route used to obtain 3D heterobimetallic MOFs. (a) Synthesis of proligands, (b) synthesis of dicopper(II) complexes and (c) synthesis of 3D MOFs.

The mentioned amino acids (**Figure I.32**) have been selected, on the basis of their different functional groups in the side chains (thioether, hydroxyl and imidazole), which may allow the design and construction of MOFs with dissimilar functional tunable pores (in terms of size, shape and reactivity). In addition, the amazing host-guest chemistry involving the interaction between MOF's channels and functional guest molecules, in combination with the possibility of using PSMs, without altering their structures, offers endless possibilities to obtain multifunctional materials for technological and environmental applications.

I.5. References

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II.

Metal-Organic Frameworks for Water Remediation

II.1. Introduction

For decades, tons of substances synthesized for agriculture, industry and domestic activities have been discharged into the environment generating severe pollution issues on the entire Earth's ecosystem,[1] being especially dramatic the effects of human activities in the Earth's water system. Water is a scarce[2] and valuable natural resource that is suffering a great deterioration as a result of population growth, rapid economic and industrial development, inadequate use of it and accidental/unauthorised/deliberate discharge of contaminants. The sources of contaminants in aquatic ecosystems are quite scattered and diverse, being the urban (*e.g.*, pharmaceutical and personal care products), industrial (*e.g.*, dyes, phthalates, phenols, nitrobenzene), agricultural (*e.g.*, herbicides, pesticides) and livestock (*e.g.*, veterinary drugs) wastewater the main ones. According to the World Health Organization (WHO), in 2015 roughly 845 million people did not have access to clean drinking water, causing a nearly 842 000 diarrheal deaths.[3]

Having access to clean freshwater is a necessary requisite for a proper development of living beings. The harvesting groundwater or desalination from seawater to obtain freshwater is a clear way to address the scarcity problems. However, they are not viable options in the short term and require means that are not available or affordable all over the world. That is why, the water reuse is becoming increasingly important, and the research community has displayed considerable interest in the development of technologies for effective and efficient removal of contaminants from water.[4]

There is a wide variety of contaminants that can be found in wastewater, some of which are toxic, carcinogenic and harmful to the environment, depending on the dose, route of exposure and chemical form. They can be classified as physical, chemical, and biological. The chemicals are divided into organic and inorganic, being the organic more biodegradable than inorganic.[5]

Among the inorganic contaminants, the most common ones are heavy metals. Traditionally, they have been widely used in multiple applications, and their deficient handling and recovery have led to a disturbing distribution in the environment. Arsenic, cadmium, chromium, lead and mercury are metals with a high degree of toxicity, which induce damage to multiple organs even at very low levels of exposure. So it is very important to eliminate them from water.[6-8] For example, lead is found in paint, solder, lead-acid batteries and ammunitions, among others, and has a cumulative effect in animal and human organs, affecting the central nervous system. Cadmium is also cumulative in the kidney and liver organs and can cause death. It is frequently used in production of alloys, pigments, and batteries. In the case of mercury, is used to manufacture switches, thermostats, batteries, in odontology and many other industrial processes. It is found in nature in elemental (Hg^0), inorganic (Hg^{1+}, Hg^{2+}) and organic (methylmercury) forms, having each species different levels of toxicity. On the other hand, there are also others metals, such as gold and silver, which recovery from water is important, although in these cases, it is mainly for its value.[9]

In addition to heavy metals, there are also other inorganic pollutants, such as inorganic acids and anions, nuclear wastes and oxyanions/cations of different metallic and non-metallic species that cause dangerous effects.

Concerning organic pollutants, there are a huge diversity of them, and their continuous production to cover the compelling demand for essential goods of advanced societies make them pseudo-persistent in our ecosystems. Among the most common ones are polycyclic aromatic hydrocarbons (PAHs), phenols, oils, greases, pharmaceuticals, phthalates, proteins, carbohydrates, dyes, detergents, pesticides and fertilizers. Generally, they are highly toxic, possible carcinogens[10] and difficult to degrade, resisting biological treatments and therefore causing serious environmental problems.[11]

For example, the increasing consumption of pharmaceutical and personal care products has led to the accumulation in water of a wide range of organic contaminants such as antibiotics, antidepressants, hormones, UV filters, fragrances and disinfectants.[12] In the case of antibiotics, its presence even at low concentrations, can cause the resistance of bacterial species to them, reducing their therapeutic potential.

The organic dyes are also very common, since they are used in many industries as textile, plastic, cosmetic, paper and food processing. In addition, there is a great variety of them, which make more difficult its removal from aquatic ecosystems.[13] They can give undesirable color to the water, being visible even at low concentrations, and reduce sunlight penetration, since they reflect or transmit the incident sunlight. Therefore, they can affect the photosynthetic activity in aquatic life, as well as being toxic due to the presence in them of metals. Besides, they can cause serious damage to humans, affecting the central nervous system, the reproductive system, and organs such as the liver. Moreover, some azo dyes may be carcinogenic or mutagenic.[14,15]

There are different methods for water remediation,[16,17] which include adsorption, filtration, coagulation, sedimentation, biological processes, advanced oxidation processes (AOPs) or chemical and membrane technologies. All of them have limitations and both their advantages and their limitations are those that define its fields of application, since some of them do not completely eliminate the waste, they can generate secondary pollutants or its operating costs are very high.

Among the water remediation methods, adsorption[18] has the advantages of being inexpensiveness and ease of operation. In this context, a recent alternative that is attracting a great interest is the use of MOFs for the adsorption of pollutants. They present high porosity, their pore size, shape and functionality can be easily tailored and show a rich host-guest chemistry, which make possible to target providing selective specific MOFs for the removal of certain contaminants.[4] In addition, MOFs have also shown potential to carry out photocatalytic degradation of pollutants.[19]

Given the great need to eliminate both organic and inorganic contaminants from water, in this section of the thesis, the preparation of four robust and water stable three-dimensional MOFs (**Figure II.1**), derived from the amino acids *L*-methionine, *L*-serine and *L*-threonine, which have functional pores capable of capturing pollutants, is presented.

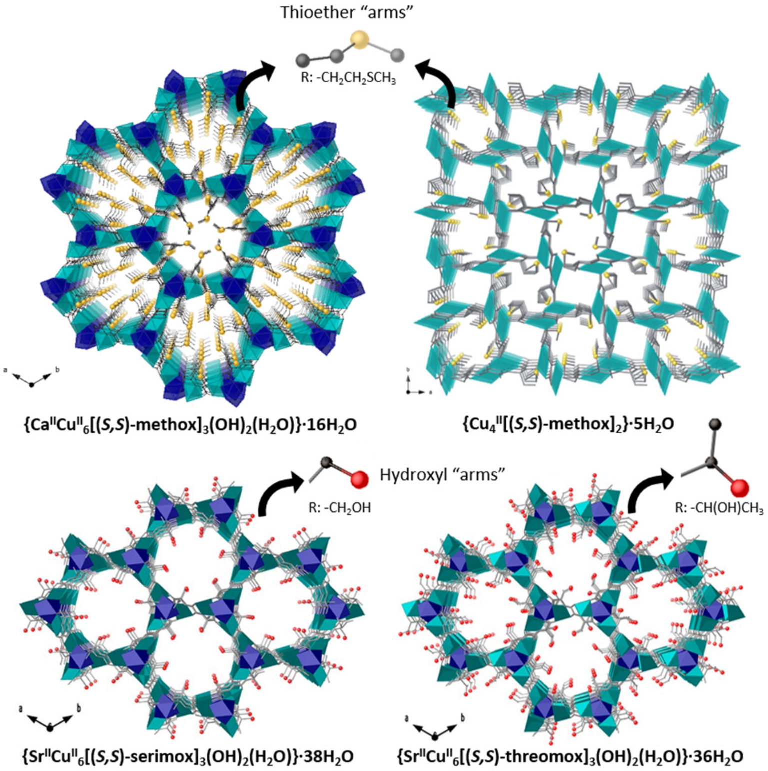

Figure II.1. Perspective views along *c* axis of the 3D porous structures synthesized from the amino acids *L*-methionine, *L*-serine and *L*-threonine. Cu and Ca or Sr atoms are represented by cyan and blue polyhedra, respectively, whereas the ligands are depicted as sticks. The sulfur and oxygen atoms are shown as yellow and red spheres, respectively.

The MOFs derived from *L*-methionine have channels decorated with accessible thioether chains, which have a high affinity for hazardous mercury species (Hg^{2+} and CH_3Hg^+) allowing to reduce the concentration of these in drinking water. In addition, the 3D calcium(II)−copper(II) network is able to recover gold from aqueous solutions given the strong affinity of this metal for the sulfur derivatives, which is very important from the economic and environmental point of view.

On the other hand, the three-dimensional MOF derived from *L*-serine, shows pores decorated with hydroxyl groups that allow the efficient removal of different organic dyes as well as different drugs (vitamins, anti-depressants and hormones), due to its ability to establish specific host-guest interactions with the organic molecules mentioned. Finally, even if this cannot be considered as water remediation, the MOFs derived from *L*-serine and *L*-threonine have also been evaluated for the separation of different lanthanoids according to their size and capability to interact with the -OH functional groups decorating the pores of these materials, showing promising results.

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Article 1.

Selective Gold Recovery and Catalysis in a Highly Flexible Methionine-Decorated Metal-Organic Framework.

Article 1

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Selective Gold Recovery and Catalysis in a Highly Flexible Methionine-Decorated Metal–Organic Framework

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Supporting Information

ABSTRACT: A novel chiral 3D bioMOF exhibiting functional channels with thio-alkyl chains derived from the natural amino acid L-methionine (**1**) has been rationally prepared. The well-known strong affinity of gold for sulfur derivatives, together with the extremely high flexibility of the thioether "arms" decorating the channels, account for a selective capture of gold(III) and gold(I) salts in the presence of other metal cations typically found in electronic wastes. The X-ray single-crystal structures of the different gold adsorbates **Au^{III}@1** and **Au^{I}@1** suggest that the selective metal capture occurs in a metal ion recognition process somehow mimicking what happens in biological systems and protein receptors. Both **Au^{III}@1** and **Au^{I}@1** display high activity as heterogeneous catalyst for the hydroalkoxylation of alkynes, further expanding the application of these novel hybrid materials.

The consumerism that modern societies have developed toward electronics devices has transformed the electronic waste into urban mines for noble metals. In particular, the recovery of gold from electronic scraps is extremely important from an economic and environmental perspective.[1] The high concentration of gold in electronic wastes has driven the quest of environmentally friendly methods for the recovery of gold from aqueous solutions. Although very few alternative methods to the highly contaminating cyanide leeching[2] have been proposed,[3,4] further advances focusing on increasing gold-selectivity and chemicals saving are mandatory.

Metal–organic frameworks (MOFs)[5−9] are porous materials showing a wide variety of thrilling chemical and physical properties and, consequently, find applications in very diverse fields.[10−15] Indeed, both MOF's porosity and their fascinating host–guest chemistry[14] lie at the origin of most of these properties. In the same way that other porous materials,[16,17] MOFs have proven their efficiency as vessels to capture and host small molecules[18] and, eventually, to separate mixtures of molecules according to their steric and stereochemical features as well as reactivity properties (functional substituent groups).[19−22]

Despite the fact that a few examples of selective metal capture by MOFs have been reported,[23] to the best of our knowledge, the important recovery of Au has not been studied. Aiming at expanding the scope of application of MOFs and taking advantage of the well-known strong affinity of gold for sulfur derivatives,[24,25] we have focused our efforts on the rational design of bioMOFs showing functional channels decorated with thio-alkyl chains derived from the natural amino acid[26] L-methionine (Scheme S1). Thus, we have synthesized a robust and water-stable 3D bioMOF of formula $\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}\cdot 16H_2O$ (**1**). The presence of thioether groups within the accessible void space of this porous material encouraged us to evaluate its selectivity for the recovery of gold. Indeed, **1** exhibited a great affinity for Au^{3+} and Au^{+} salts (such as $AuCl_3$ and AuCl) in water, even in the presence of a wide variety of other metal cations regularly present in electronic wastes ("e-wastes") like Pd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Al^{3+}, yielding the novel compounds $(AuCl_3)_3@\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}\cdot 9H_2O$ (**Au^{III}@1**) and $(AuCl)_2@\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}\cdot 3H_2O\cdot 3CH_3OH$ (**Au^{I}@1**) (see Supporting Information (SI)).

Compound **1** was synthesized as green hexagonal prisms with a slow diffusion technique (see experimental section in the SI). Thereafter, in order to find out the maximum gold uptake capacity, we suspended 5 mg of **1** in 5 mL of a 0.02 M $AuCl_3$ H_2O/CH_3OH (1:1) solution to obtain **Au^{III}@1**. ICP-AES and SEM analyses indicated a maximum loading of 3 mmol of Au(III) per mmol of MOF after 1 h, which remained invariable after further time suspension. This indicates a total recovery of 598 mg of $AuCl_3$ per g of MOF in **Au^{III}@1**. The same procedure was repeated by soaking 5 mg of **1** in 5 mL of a 0.02 M AuCl aqueous solution. A maximum uptake of two mmol of AuCl per mmol of MOF was achieved after 3 h. The calculated total recovery of 300 mg of AuCl per g of MOF in **Au^{I}@1** is almost half-fold to that of **Au^{III}@1**.

The crystal structures of **1**, **Au^{III}@1** and **Au^{I}@1** could be determined by single-crystal X-ray diffraction (XRD) (see SI for structural details). They crystallize in the chiral $P6_3$ space group

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Selective Gold Recovery and Catalysis in a Highly Flexible Methionine-Decorated Metal-Organic Framework

Marta Mon, Jesús Ferrando-Soria, Thais Grancha, Francisco R. Fortea-Pérez, Jorge Gascon, Antonio Leyva-Pérez,* Donatella Armentano* and Emilio Pardo*

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Article 2.

Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF.

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Mercury

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Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF

Marta Mon, Francesc Lloret, Jesús Ferrando-Soria, Carlos Martí-Gastaldo, Donatella Armentano,* and Emilio Pardo**

Abstract: *A robust and water-stable metal–organic framework (MOF), featuring hexagonal channels decorated with methionine residues (**1**), selectively captures toxic species such as CH_3Hg^+ and Hg^{2+} from water. **1** exhibits the largest Hg^{2+} uptake capacity ever reported for a MOF, decreasing the [Hg^{2+}] and [CH_3Hg^+] concentrations in potable water from highly hazardous 10 ppm to the much safer values of 6 and 27 ppb, respectively. Just like with biological systems, the high-performance metal capture also involves a molecular recognition process. Both CH_3Hg^+ and Hg^{2+} are efficiently immobilized by specific conformations adopted by the flexible thioether "claws" decorating the pores of **1**. This leads to very stable structural conformations reminiscent of those responsible for the biological activity of the enzyme mercury reductase (MR).*

Even though the WHO is strongly trying to raise awareness for reducing the amount of mercury in domestic tools and in different industrial sectors (e.g., chloralkali plants and vinyl chloride monomer production),[1] the world's annual mercury consumption was still estimated to be up to 2000 tons in 2016.[2] Environmental contamination by the interconvertible[3,4] Hg^{2+} and CH_3Hg^+ cations is of great concern from the viewpoint of human health.[5] In this sense, the very easy air and water transportation of both species, as well as their long atmospheric lifetimes, make them very widespread environment pollutants.[6] As a consequence, high concentrations of mercury can be found not only in fish,[7] but also in agricultural crops[8] and in animals living in non-marine habitats.[9] On this basis, the search for sustainable green methods for the effective capture and removal of the different chemical forms of mercury is mandatory and has attracted a great deal of interest.[10–15]

Metal–organic frameworks (MOFs)[16–20] have already been shown to perform very well in the selective capture and/or separation of gases,[21] metals,[22] and small molecules.[23] Most of these thrilling properties of MOFs, which are related to their porous character and rich host–guest chemistry,[24] can be tuned by an appropriate functionalization of the channels. Taking advantage of the methods provided by coordination chemistry, an accurate design effort[25] should thus lead to water-stable[26,27] MOFs for use as "mercury receptors".[28–33]

Nature has evolved mechanisms to effectively distinguish one metal from another. How metal ions move to and from their target destinations in the active site of a metalloenzyme, or as structural components of other biomolecules such as nucleic acids, efficiently contributes to the regulation of biological processes. An interesting example within this context is the mercury reductase (MR),[34] a redox enzyme that catalyzes the reduction of highly toxic Hg^{2+} into more benign Hg^0. The active center of this enzyme represents a source of inspiration for coordination chemists working in the area of mercury detoxification, and efforts trying to mimic it have been pursued.[34] MOFs could thus also find application as vessels encapsulating biological systems.[35]

Among the large class of MOFs, bioMOFs,[36] designed from naturally occurring organic ligands, are highly promising for both mercury removal and biomimicry. In this context, we have recently reported a robust and water-stable, heterobimetallic calcium(II)/copper(II) three-dimensional (3D) bioMOF,[37] which was synthesized by using the enantiopure bis[(*S*)-methionine]oxalyl diamide[37–40] ligand derived from the natural amino acid L-methionine (see the Supporting Information, Scheme S1). This porous material with the formula $\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}\cdot 16\,H_2O$ (**1**) features functional channels decorated with thioalkyl chains, which account for its strong and selective affinity for different gold salts as well as excellent catalytic activity.[37] On the basis of the well-known affinity of mercury for sulfur atoms, we have further extended this work to evaluate the efficiency of **1** in the capture and removal of Hg^{2+} and CH_3Hg^+ from aqueous media (Scheme S2). The high selectivity and capture capacity of **1** towards these hazardous species from aqueous solutions render it a good mercury removal agent, expanding the concept of "metal receptors" from biology to nanotechnology applications.

We began our study by investigating the efficiency of **1** in the capture of $HgCl_2$ and CH_3HgCl salts from water. However, its maximum loading capacity was determined from water and water/methanol, respectively. Thus crystals of **1** were soaked in saturated solutions of $HgCl_2$ (H_2O) and

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Supporting Information

Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF

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Article 3.

Fine-Tuning of the Confined Space in Microporous Metal-Organic Frameworks for Efficient Mercury Removal.

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Fine-tuning of the confined space in microporous metal–organic frameworks for efficient mercury removal†

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Offsetting the impact of human activities on the biogeochemical cycle of mercury has become necessary for a sustainable planet. Herein, we report the development of a water-stable and eco-friendly metal–organic framework, which has the formula $\{Cu_4^{II}[(S,S)\text{-methox}]_2\}\cdot 5H_2O$ (**1**), where methox is bis[(*S*)-methionine]oxalyl diamide. Its features include narrow functional channels decorated with thioalkyl chains, which are able to capture $HgCl_2$ from aqueous media in an efficient, selective, and rapid manner. The conscious design effort in terms of size, shape, and reactivity of the channels results in extremely efficient immobilization of $HgCl_2$ guest species in a very stable conformation, similar to that of the enzyme mercury reductase. Thus, **1** enables the highly efficient removal of toxic $HgCl_2$ from aqueous media and reduces the $[Hg^{2+}]$ concentration from the dangerous level of 10 ppm to acceptable limits of below 2 ppb in drinking water. The unusual combination of a low-cost straightforward synthetic procedure and high stability under environmental conditions, together with its ability to efficiently and rapidly remove poisonous mercury ions, places **1** among the most attractive adsorbents reported to date for the purification of contaminated water.

Metal–organic frameworks (MOFs)[1–5] have attracted significant attention in recent years due to their wide range of functional properties.[6] Among them, the selective capture and/or separation of gases[7] and small molecules[8] of relevance are significant from an industrial and ecological point of view. Their excellent performances are attributed to the exclusive combination of fascinating host-guest chemistry[9–16] and high crystallinity, which confer MOFs with unparalleled synthetic versatility, as evidenced by X-ray crystallography. This synthetic versatility has allowed improvement in their capture/separation properties by chemically engineering MOF channels with appropriate size, shape, and reactivity,[17] or by post-synthetic modification.[18,19] To date, this enormous synthetic potential has already resulted in numerous MOFs for the separation of different gases of importance in both industrial and environmental fields.[20–22] Conversely, molecular recognition with MOFs has scarcely been explored. Some promising results[23,24] have shown the potential of MOFs in this area; however, the encapsulation and separation of complex molecular systems still need to be investigated.[1]

One of the greatest challenges the world faces today is the increasing heavy metal pollution caused by industrial activities and/or accidental discharge. In particular, highly toxic mercury derivatives are widespread in the environment[25–28] such as in air, water, and soil,[29,30] which are a threat to public health. Therefore, it is urgent to develop novel efficient methods to selectively capture mercury;[31–37] currently, MOFs are showing potential as very attractive materials in this area.[38–44]

Bioinspired MOFs, in which the linker is evocative of the bioworld, possess the advantages of environmentally friendly designs and the intrinsic capabilities of biomolecules to drive molecular recognition processes owing to the presence of several accessible metal binding sites and intrinsic ability to self-organize into highly ordered structures through hydrogen bonding, π-stacking or coordination-driven self-assembly interactions. This enables the design and synthesis of bioMOFs with tailorable and highly task-specific functionalities.

In this study, we synthesised a new water-stable microporous MOF with very narrow square functional channels, which are decorated with thioether groups (Scheme 1 and Fig. 1). We report the synthesis and characterization of this novel three-dimensional bioMOF,[45,46] which is prepared from an oxamidato-based ligand[42,47,48] derived from the natural amino acid methionine, has the formula $\{Cu_4^{II}[(S,S)\text{-methox}]_2\}\cdot 5H_2O$

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pp. 144-162

Article 4.

Crystallographic Snapshots of Host-Guest Interactions in Drugs@Metal-Organic Frameworks: Towards Mimicking Molecular Recognition Processes.

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Crystallographic snapshots of host–guest interactions in drugs@metal–organic frameworks: towards mimicking molecular recognition processes†

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We report a novel metal–organic framework (MOF) featuring functional pores decorated with hydroxyl groups derived from the natural amino acid L-serine, which is able to establish specific interactions of different natures, strengths and directionalities with organic molecules of technological interest, *i.e.* ascorbic acid, pyridoxine, bupropion and 17-β-estradiol, based on their different sizes and chemical natures. The ability of 1 to distinctly organize guest molecules within its channels, through the concomitant effect of different directing supramolecular host–guest interactions, enables gaining unique insights, by means of single-crystal X-ray crystallography, into the host–guest interactions. These results increase our understanding of molecular recognition processes in MOFs, opening a myriad of potential technological applications in the near future.

Conceptual insights

Molecular recognition processes based on host–guest interactions are ubiquitous in biological systems. Understanding these processes is pivotal to mimicking such complex functions and developing materials with potential technological applications. Metal–Organic Frameworks (MOFs), due to their rich host–guest chemistry and high crystallinity, have emerged as potential platforms to shed light on this challenging task. Recently, the crystalline sponge method has made revelation of the structures of guest molecules by X-ray diffraction possible, exploiting MOFs' ability to host and align these moieties within their pores. However, it is mainly based on scaffolds which take advantage of hydrophobic–hydrophilic host–guest interactions. In this communication, we add a new concept of broad interest to achieve a better understanding of molecular recognition, based on the development of a novel MOF with hydrogen bonding sites confined within pores, intrinsically devoted towards hosting and imparting supramolecular order to guest molecules in a manner reminiscent of bio-molecular recognition. Assisted by X-ray crystallography, we have demonstrated its ability to act as a receptor distinctly organizing organic molecules of bio-technological interest. It allows achieving an unprecedented correlation of the magnitude of the host–guest interactions with the uptake and stimuli-responsive release properties, paving the way for a more conscious design of new bio-carrier materials.

Solid porous materials have inner functional cavities offering unique possibilities in catalysis, adsorption and separation or ion exchange processes.[1] Among them, the so-called metal–organic frameworks (MOFs)[2–8] – hybrid materials consisting of metal cations or clusters linked by an almost limitless number of possible organic linkers – have experienced incredibly fast growth in recent years. Reasons for such interest include (i) amazing host–guest chemistry,[2] based on the shape, size and function of the cavities, and further improved by the overall flexibility and adaptability of the framework,[9] (ii) the capability to precisely tailor such inner spaces, either pre- or post-synthetically,[10–13] and, (iii) last but not least, the possibility of using single-crystal X-ray crystallography, as a powerful tool to directly shed light on the nature of the resulting host–guest interactions.[14]

Since the publication of several pioneering studies proving the extraordinary host–guest chemistry of MOFs,[15–18] many groups have devoted their efforts towards attempting the reversible encapsulation of guest molecules, while maintaining the MOFs' crystallinity.[19–21] Despite the progress made in the search for applications, much work remains to be done in the realm of MOF chemistry – in particular, in terms of molecular recognition and/or encapsulation of more complex molecular systems,[22–26] as well as mimicking the specific host–guest interactions and molecular recognition processes shown by molecular cages in solution,[27] and especially, on the structural characterization of such hybrid host–guest systems.[28]

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Marta Mon, Rosaria Bruno, Jesús Ferrando-Soria,* Lucia Bartella,
Leonardo Di Donna, Marianna Talia, Rosamaria Lappano,
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pp. 174-202

Article 5.

Efficient Capture of Organic Dyes and Crystallographic Snapshots by a Highly Crystalline Amino Acid-Derived Metal-Organic Framework.

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Metal–Organic Frameworks | *Hot Paper* |

Efficient Capture of Organic Dyes and Crystallographic Snapshots by a Highly Crystalline Amino-Acid-Derived Metal–Organic Framework

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Abstract: The presence of residual organic dyes in water resources or wastewater treatment systems, derived mainly from effluents of different industries, is a major environmental problem with no easy solution. Herein, an ecofriendly, water-stable metal–organic framework was prepared from a derivative of the natural amino acid L-serine. Its functional channels are densely decorated with highly flexible L-serine residues bearing hydroxyl groups. The presence of such a flexible and functional environment within the confined environment of the MOF leads to efficient removal of different organic dyes from water: Pyronin Y, Auramine O, Methylene Blue and Brilliant Green, as unveiled by unprecedented snapshots offered by single-crystal X-ray diffraction. This MOF enables highly efficient water remediation by capturing more than 90 % of dye content, even at very low concentrations such as 10 ppm, which is similar to those usually found in industrial wastewaters. Remarkably, the removal efficiency is improved in simulated contaminated mineral water with multiple dyes.

Introduction

The extensive use of organic dyes in industries as diverse as printing, paper, textile, plastic, leather, food, and pharmaceutical leads to an annual world production of 70 000 t of these organic compounds,[1] of which about 2–10 % is discharged into the aquatic system.[2] Apart from the obvious negative visual impact,[3] these polluting discharges cause irreparable ecological damage and are a threat to living beings owing to their toxicity and carcinogenicity.[1] First, the photosynthetic activity—the basis of aquatic life—is hampered in areas affected by organic dye spills, as light penetration is severely reduced.[4] Second, organic dyes are often carcinogenic, mutagenic, or teratogenic. This constitutes a serious health threat to fish and humans.[1] Consequently, many efforts are devoted to the development of new technologies to remove organic dyes from wastewater streams, preferably selectively.

Among the different methods proposed for water remediation,[5] which include coagulation/flocculation, precipitation, membranes, biological processes, advanced oxidation processes (AOPs), and adsorption by porous sorbents,[5,6] the use of metal–organic frameworks[7–14] (MOFs) for the capture and/or degradation (by AOPs) of the contaminants is one of the most promising technologies. This type of porous crystalline materials[15–17] showing host–guest chemistry[18–20] allows for greater control of their porosity in terms of size, shape, and functionality compared with other porous materials. Thus, they enable the creation of an appropriate environment for the capture of specific contaminants. Indeed, a good number of MOFs show efficient, and sometimes selective, adsorption and/or degradation through AOPs[21] of both inorganic and organic contaminants.[22–31] In particular, the use of MOFs for the elimination of organic dyes from water has been explored, and several examples of MOFs that can degrade dyes by means of AOPs have been reported,[21] as well as water-resistant functional MOFs capable of capturing anionic and/or cationic organic dyes, sometimes in a selective manner, from water.[32–49]

However, despite the progress made, much work remains to be done to rationalize the host–guest interactions responsible for the remediatory behavior of MOFs, which eventually will allow the efficiency of dye removal to be improved, particularly at the very low concentrations (parts per million level) typical of nonaccidental industrial discharges. In this respect, soft electrostatic interactions and ion-exchange processes are the main adsorption mechanisms for dye uptake.[32,33,42–48] However, these approaches often limit their use to the capture of ionic species of complementary charge to the MOF and consequent-

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Efficient capture of organic dyes and crystallographic snapshots by a highly crystalline amino acid-derived metal-organic framework

Marta Mon, Rosaria Bruno, Estefanía Tiburcio, Pierre-Edouard Casteran, Jesús Ferrando-Soria,* Donatella Armentano* and Emilio Pardo*

pp. 214-230

Article 6.

Lanthanide Discrimination with Hydroxyl-Decorated Flexible Metal-Organic Frameworks.

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Lanthanide Discrimination with Hydroxyl-Decorated Flexible Metal−Organic Frameworks

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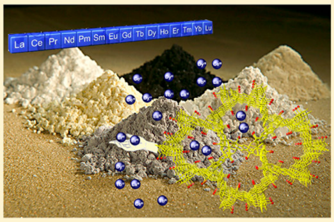
Supporting Information

ABSTRACT: We report two new highly crystalline metal−organic frameworks (MOFs), derived from the natural amino acids serine (**1**) and threonine (**2**), featuring hexagonal channels densely decorated with hydroxyl groups belonging to the amino acid residues. Both **1** and **2** are capable of discriminating, via solid-phase extraction, a mixture of selected chloride salts of lanthanides on the basis of their size, chemical affinity, and/or the flexibility of the network. In addition, this discrimination follows a completely different trend for **1** and **2** because of the different locations of the hydroxyl groups in each compound, which is evocative of steric complementarity between the substrate and receptor. Last but not least, the crystal structures of selected adsorbates could be resolved, offering unprecedented snapshots on the capture process and enabling structural correlations with the separation mechanism.



INTRODUCTION

Lanthanides are elements of essential importance[1] with a key role in many important fields,[2] but their very similar size and chemical properties greatly complicate their separation. Today, the separation of lanthanides is mainly carried out by solvent-extraction methods,[3] although other techniques such as chromatographic separation,[4] fractional crystallization,[5] or ion exchange[5] have also been evaluated. However, these methods require many steps, which eventually drives up production costs. In this context, the search for simpler and less-costly methods still continues.[6]

Metal−organic frameworks (MOFs)[7−11] are an emerging type of porous crystalline materials that have find applications in many different important fields.[9,12,13] In particular, their use in the selective capture and/or separation of gases[14,15] and even small molecules,[16] driven by their porous nature and rich host−guest chemistry,[17−24] is very relevant from both ecological and industrial perspectives. Initially, in MOFs and other porous materials, molecular sieving,[25] where shape/size selectivity determined which molecules can access the porosity, was considered to be the only key factor accounting for such separations. However, other unique characteristics of MOFs, such as flexibility[19,26,27] and adaptability,[28−30] together with the tunable functionality of the channels, have proven to be important in this respect because it has been underpinned with the precious help of X-ray crystallography.[31−35] In fact, MOFs have shown promising results, for example, in the selective capture of metals,[36−38] separation of organic molecules,[39] and even encapsulation and structure resolution of molecules of unknown structure.[40]

Despite this great potential, the applicability of MOFs in lanthanide separation has only been barely explored, and the very few reported works on this subject are focused on their size-selective crystallization properties.[41−44] In this work, we investigate the possibility of achieving postsynthetic lanthanide discrimination,[45] via solid-phase extraction (SPE), using MOFs with both appropriate functional groups capable of retaining lanthanides and flexibility to enable recognition based on the ionic radii and chemical affinity.

RESULTS AND DISCUSSION

Synthesis and X-ray Crystal Structure. Here, we report two novel chiral three-dimensional (3D) MOFs, prepared using ligands derived from the natural amino acids L-serine and L-threonine, both featuring functional channels decorated with hydroxyl (−OH) groups, with the formulas $\{Sr^{II}Cu^{II}_6[(S,S)\text{-serimox}]_3(OH)_2(H_2O)\}\cdot 38H_2O$ (**1**) and $\{Sr^{II}Cu^{II}_6[(S,S)\text{-threomox}]_3(OH)_2(H_2O)\}\cdot 36H_2O$ (**2**) (where serimox = bis[(*S*)-serine]oxalyldiamide[34] and threomox = bis[(*S*)-threonine]oxalyldiamide; Scheme 1 and Figures 1, 2, and S1−S3). The presence of hydroxyl groups pointing toward the accessible void space of the MOF (Figure 1), together with the high flexibility of these types of amino acid based MOFs,[36,37] provides an adaptable functional environment capable of interacting with lanthanides.

Compounds **1** and **2** were synthesized as green hexagonal prisms with a slow diffusion technique (see the Supporting

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Lanthanide Discrimination with Hydroxyl-Decorated Flexible Metal-Organic Frameworks

Marta Mon,[†] Rosaria Bruno,[§] Rosangela Elliani,[§] Antonio Tagarelli,[§] Xiaoni Qu,[‡,†] Sanping Chen,[‡] Jesús Ferrando-Soria,*[,†] Donatella Armentano*[,§] and Emilio Pardo*[,†]

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Article 7.

Metal-Organic Framework Technologies for Water Remediation: Towards a Sustainable Ecosystem.

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Metal–organic framework technologies for water remediation: towards a sustainable ecosystem

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Having access to clean water is a mandatory requirement for the proper development of living beings. So, addressing the removal of contaminants from aquatic systems should be a priority research topic in order to restore ecosystem balance and secure a more sustainable future. The fascinating structures and striking physical properties of metal–organic frameworks (MOFs) have revealed them as excellent platforms for the removal of harmful species from water. In this review, we have focused our attention on critically highlighting the latest developments achieved in the adsorptive removal of inorganic – metal cations, inorganic acids, oxyanions/cations, nuclear wastes and other inorganic anions – and organic – pharmaceuticals and personal care products, artificial sweeteners and feed additives, agricultural products, organic dyes and industrial products – contaminants commonly found in wastewater using MOF technologies. In particular, we have attempted to give a clear insight into the different synthetic strategies for water remediation, stressing the wide tunability of MOFs. For this purpose, we have classified these two kinds of pollutants into different subfamilies, based on their chemical composition or common use. Finally, we have proposed some future trends and challenges that need to be addressed for widening the range of applicability of MOFs and making solid headway towards sustainable development.

1. Introduction

Human activities since the advent of the industrial revolution have generated a deep negative impact on the Earth's ecosystem.[1] The continuous growth of world population together with the increase of energy and commodity consumption threatens the sustainability of life on Earth for future generations.[2] Covering the compelling demand for essential goods of modern societies is leading to unprecedented amounts of hazardous wastes.[3] Nowadays, the first consequences of this environmental pollution and overexploitation of natural resources are more than evident in the Earth's water system (Fig. 1).[4] Currently, nearly half of the world's population is living in water stressed areas, and it is projected to get worse in the following decades with the increase in global temperatures as a consequence of global warming. In fact, providing universal access to clean freshwater is one of the main goals of the Sustainable Development Agenda of the United Nations.[5]

Freshwater harvesting from groundwater and desalination of seawater appear, *a priori*, as the natural options to circumvent the world's water crisis.[6] However, the technologies needed to perform it in an efficient manner are not affordable all over the world.[7] In addition, overexploitation of aquifers, ultimately, can lead to drawdown or saltwater intrusion, and desalinization plants could also become a source of contamination of coastal waters. In this context, it is mandatory to raise awareness of the

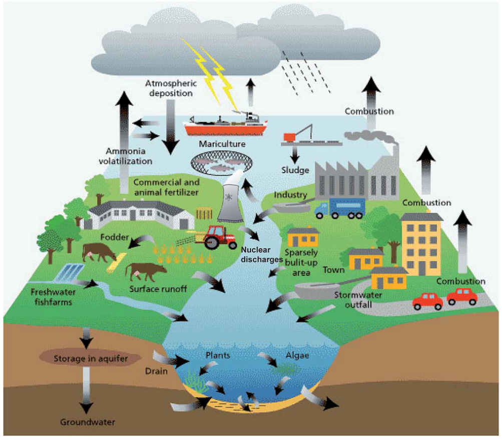

Fig. 1 Sources of groundwater contamination in the hydrologic cycle.

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III.

Post-Synthetic Methods in Metal-Organic Frameworks: Towards New Applications

III.1. Introduction

Post-synthetic methods (PSMs) have proven to be very useful chemical tools for the design of novel advanced materials.[1-4] These methods allow improving physical or chemical properties of preformed MOFs, or even provide new ones, preserving the structural integrity and porosity of the framework. In addition, PSMs offer the possibility of using the pores of the MOFs as templates to synthesize functional species, otherwise not accessible.

The term “post-synthetic” refers to the fact that the modifications are performed after the MOF has already been obtained, which is very useful in cases that the incorporation of desired chemical functionalities via direct synthesis is not possible. Remarkably, due to the high crystallinity of MOFs, these PSMs can be performed in a single-crystal to single-crystal (SC to SC) manner. In MOFs, this methodology is widely employed, since its high porosity allows access of the reagents to the interior of these solids, being possible to carry out the functionalization both of the interior and the exterior of the material. Furthermore, the fact that MOFs are constituted by organic ligands makes it possible to employ a huge diversity of post-synthetic organic transformations, introducing a rich chemical functionality in these materials.

There are a great variety of ways to modify MOFs after their preparation, and even its desolvation can be considered a type of post-synthetic modification. Therefore, the choice of one type or another will depend on the functionality or application, with which it is intended to endow the material, being possible to use more than one modification in the same material.

The most common post-synthetic modifications (**Figure III.1**) performed in MOFs are described hereunder:

- Covalent PSM consists of the formation of a new covalent bond, usually in the organic ligand of the MOFs (**Figure III.1a**),[5] although it could also occur in the secondary building units (SBUs). This method has proven to be a good option to introduce chemical groups in MOFs. For example, from amines[6] or aldehydes[7] present in the structures, different reactions can be carried out to obtain other functional groups.

- Post-synthetic deprotection (PSD), is based on the cleavage of a chemical bond. That is, the MOFs are formed using an organic linker that has a protected functional group and after its synthesis, the protecting group is removed.[5,8]

- Post-synthetic polymerization (PSP) has as aim to transform MOFs into polymer materials or into polymer-MOF composites. This modification could be carried out, for example, by means of multiple organic reactions to connect the ligands building the MOF within each other[9] (**Figure III.1h**) or by growth of the polymer on the surface of the MOF.[10]

- In dative PSM, the transformation is produced by formation of dative bonds such as metal-ligand bonds. It includes the metalation of MOFs through their organic ligands, in the case of having sites that are open to the insertion of metals,[11] the formation of open metal sites in SBUs by desolvation, followed by coordination of organic species,[12] the replacement of the SBU metal ions[13] and so on. Therefore, this category includes the post-synthetic insertion (PSI) and post-synthetic exchange (PSE).

In PSI, ligands are incorporated to occupy open metal sites or labile sites on SBUs (**Figure III.1c**),[12,14,15] and the metal ions are inserted to decorate existing SBUs[16] (**Figure III.1d**) or even to metalate the organic ligands[11] (**Figure III.1b**). In particular, to refer to the first case, the term solvent-assisted linker incorporation (SALI) is also used.[17]

On the other hand, PSE is based on the replacement of ligands[18] (**Figure III.1e**) or metal components[13] (**Figure III.1f**) within the network by other components that are present in a solution (metal ions or ligands).[19] To refer, in particular, to the exchange of the ligand, is usually utilized the term solvent-assisted linker exchange (SALE).[18] It should be noted that the exchange of metal, also called as cation exchange or transmetalation, can be produced in both the likers and in the SBUs.[20]

- Last but not least, are the non-covalent post-synthetic transformations, which include the introduction or exchange of guest molecules hosted in the pores by diffusion (**Figure III.1g**).[21] As for example, growth or encapsulation of metal nanoparticles and clusters,[22-24] or in the case of anionic MOFs, exchange of extra-framework charge balancing cations by cationic metal complexes.[25,26]

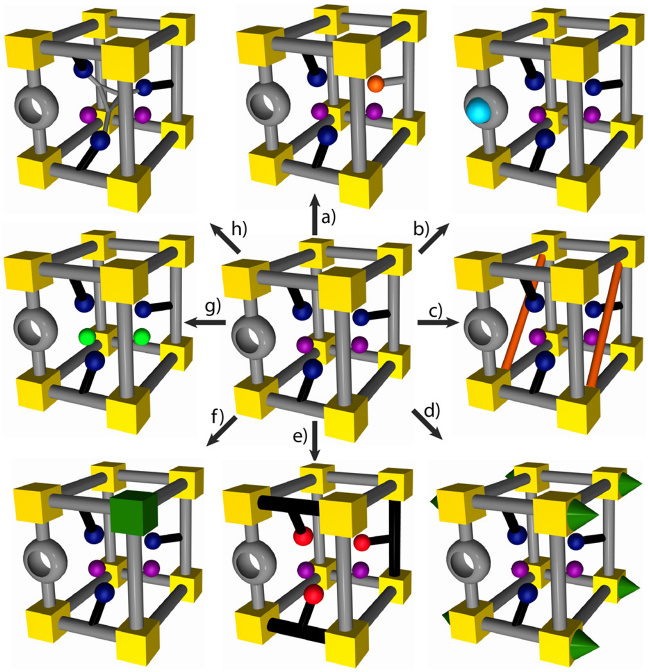

Figure III.1. Representation of the most common post-synthetic modifications in MOFs: (a) covalent PSM of ligands, (b) metalation of ligands, (c) PSI of ligands in SBUs, (d) PSI of metal ions in SBUs, (e) PSE of ligands, (f) PSE of metal components, (g) exchange of guest molecules and (h) PSP.

The fact that there are a large number of strategies to modify MOFs after their synthesis, makes it possible to obtain very versatile materials with predetermined properties for different applications. In our group, some of these methods have been widely used, as the exchange of ions constituting the coordination network,[27] as well as the ions hosted in the pores (**Figure I.29**)[28] or the encapsulation of preformed transition metal complexes,[29] allowing to obtain more stable and robust materials in which their magnetic and gas sorption properties have been improved.

In this part of the thesis, we have used PSMs with the aim of not only improving the existing properties of the synthesized compounds, but also providing new ones. We will show different reported examples, which allows us to give an overview of the multiple possibilities offered by this methodology, generating functional materials that can be used effectively in areas such as gas adsorption, ferroelectricity or as will be detailed in the following section, in catalysis.

In particular, two different anionic MOFs have been modified by straight diffusion of cationic species and the corresponding displacement of the countercations that occupy the pores. One of the MOFs used, has been obtained from the ligand derived from the amino acid *L*-histidine, following the synthetic strategy described above, and the other was obtained from an oxamate ligand, previously reported by members of the group.[27]

The channels of each MOF represent a singular playground. Thus, it is necessary to select properly both the MOFs (in terms of architecture, space group and properties) and the modifications to be made, depending on the application that is intended to give the material. For example, in order to obtain a ferroelectric material, firstly, it has been obtained a MOF using an enantiopure ligand derived from a chiral amino acid. This will allow transmitting efficiently the chiral information from the organic ligands to the final network, and eventually, getting a polar space group compatible with ferroelectricity. Then, a molecule with a strong dipole moment is incorporated within the MOFs channels, by exchange with the countercations hosted in the pores.

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Article 8.

Postsynthetic Approach for the Rational Design of Chiral Ferroelectric Metal-Organic Frameworks.

Article 8

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Postsynthetic Approach for the Rational Design of Chiral Ferroelectric Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Ferroelectrics (FEs) are materials of paramount importance with a wide diversity of applications. Herein, we propose a postsynthetic methodology for the smart implementation of ferroelectricity in chiral metal–organic frameworks (MOFs): following a single-crystal to single-crystal cation metathesis, the Ca^{2+} counterions of a preformed chiral MOF of formula $Ca_6^{II}\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 212H_2O$ (**1**), where hismox is a chiral ligand derived from the natural amino acid L-histidine, are replaced by $CH_3NH_3^+$. The resulting compound, $(CH_3NH_3)_{12}\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 178H_2O$ (**2**), retains the polar space group of **1** and is ferroelectric below 260 K. These results open a new synthetic avenue to enlarge the limited number of FE MOFs.

Ferroelectric (FE) materials[1,2] show a spontaneous electric polarization that can be switched by an external electric field *E*. They attract much interest as they can find a wide variety of important applications.[2] Most of FE materials synthesized so far[3−8] have been identified by a benchmark of the materials crystallizing in polar space groups, compatible with ferroelectricity. However, the development of more rational synthetic methodologies targeting such materials is still challenging.

Metal–organic frameworks (MOFs)[9] appear as good candidates to reach this goal: they are porous crystalline materials that exhibit both, a large diversity of captivating high-dimensional (porous) structures and exciting properties.[10] The uniqueness of MOFs resides on the possibility to combine a precise determination of their crystal structure and a rich host–guest chemistry.[10] So, MOFs are, *a priori*, the perfect playgrounds to carry out a molecular approach for the synthesis of molecule-based FEs or multiferroics (MFs).[11,12]

Nonetheless, the global strategy based on the direct synthesis of MOFs with flexible open-framework structures capable to host and align in their void spaces the dipolar guest molecules usually required to develop ferroelectricity has only led to a limited number of FE[13−17] and/or MF[18−24] MOFs. This limited efficiency is related to the necessary conditions to observe ferroelectricity such as a large polarizability of the guest molecules (although ferroelectricity can be also observed using nonpolar molecules in certain circumstances[1]) and a polar space group.[4]

Aiming to overcome such current synthetic limitations, we propose a programmed postsynthetic strategy[25] for the rational design of FE materials. The first step of this approach is the selection of a MOF with the appropriate polar space group. The second step is a solid-state single-crystal to single-crystal (SC to SC) process allowing to insert, into the preformed MOF, molecules with a strong dipolar moment *P*. The polar space group of the MOF would actually impose a non-centrosymmetric organization of the molecules, avoiding the cancellation of the macroscopic polarization most often observed during the direct crystallization of polar molecules.[26]

Herein, the selected polar MOF is a novel chiral oxamidato-based[27−29] *bio*MOF, of formula $Ca_6^{II}\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 212H_2O$ (**1**) [H_2Me_2-(*S*,*S*)-hismox = bis[(*S*)-histidine]oxalyl diamide, Scheme S1a]. The dipolar molecule is the versatile $CH_3NH_3^+$. The process is a solid-state postsynthetic[25] metathesis, where the Ca^{2+} cations are replaced by the polar $CH_3NH_3^+$ ones, which are known to be favorable for the occurrence of ferroelectricity.[22] It yields a new MOF of formula $(CH_3NH_3)_{12}\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 178H_2O$ (**2**) (see Experimental Section, Supporting Information). It preserves the polar space group of **1** (see structural section), creates the appropriate environment for the polar $CH_3NH_3^+$ cations and opens the gate for the observation of ferroelectric properties. This postsynthetic strategy appears a rational method toward molecular FE materials giving, *a priori*, highest chances to observe FE properties.

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A Postsynthetic Approach for the Rational Design of Chiral Ferroelectric Metal-Organic Frameworks

Marta Mon, Jesús Ferrando-Soria, Michel Verdaguer, Cyrille Train,
Charles Paillard, Brahim Dkhil, Carlo Versace, Rosaria Bruno,
Donatella Armentano* and Emilio Pardo*

pp. 320-344

Article 9.

A Post-Synthetic Approach Triggers Selective and Reversible Sulphur Dioxide Adsorption on a Metal-Organic Framework.

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A post-synthetic approach triggers selective and reversible sulphur dioxide adsorption on a metal–organic framework†

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We report the application of a post-synthetic solid-state cation-exchange process to afford a novel 3D MOF with hydrated barium cations hosted at pores able to trigger selective and reversible SO_2 adsorption. Computational modelling supports the full reversibility of the adsorption process on the basis of weak supramolecular interactions between SO_2 and coordinated water molecules.

The efficient capture and sequestration of flue-gas emissions derived from fossil fuel combustion represents one of the greatest global challenges.[1] This has become an even more critical issue with the widespread use of low-grade fossil fuels,[2] whose high sulphur content has considerably contributed to increases in the levels of sulphur dioxide (SO_2) in the Earth's atmosphere well above 8 ppb recommended by the World Health Organization (WHO).[3] The selective removal of SO_2 from post-combustion flue-gas emission is of two-fold fundamental importance: (i) the direct high impact on the global air quality, and the consequent environmental burden (*i.e.* smog and acid rain) and risk for human health,[4] and (ii) the detrimental effect of SO_2 on the removal processes of other components of flue-gas, such as CO_2 and NO_x.[5]

Currently, flue-gas desulfurization (FGD) is performed mainly by wet scrubbing with limestone slurry or *via* a wet sulphuric acid process.[6] However, these processes require large amounts of water and further treatment of the resultant waste-water, and most importantly, they are able to remove only 90–95% SO_2. Thus, the discovery of new materials able to achieve deep desulfurization is mandatory to move towards a green economy and a sustainable environmental development.

Metal–organic frameworks (MOFs)[7] are porous crystalline materials with a wide range of applications.[7,8] To a large extent, this is mainly a consequence of the combination of two unique features: (i) exquisite fine control over the size, shape and functionality of the MOF's channels using rational design strategies[9] and/or post-synthetic methodologies (PSMs)[10] and (ii) the possibility of using X-ray crystallography to understand the physical/chemical processes inside their pores.[11] Overall, this has made MOFs unique among other porous materials to outperform current technologies. This point has been clearly reflected in the considerable advances made in the selective capture and/or separation of light hydrocarbons,[12] toxic and greenhouse gases,[13] metals and small molecules.[14] However, this is not yet the case for the selective adsorption of SO_2 at low partial pressures from post-combustion flue-gas, where studies, compared to other gases such as CO_2, are still scarce.[15] This is most-likely related to the limited stability of MOFs to the highly corrosive and reactive nature of SO_2, and to the lower SO_2 concentration in flue-gas than N_2 and CO_2 (the typical composition of flue gas from coal combustion: N_2 = 70–75%; CO_2 = 10–15%; SO_2 = 500–3000 ppm), which make the total desulfurization of flue gas a very challenging task.[16] Nevertheless, some relevant advances have been made in the selective adsorption of SO_2.[15] The most remarkable ones have been based on the careful design of ultra-stable MOFs with relatively small pores either decorated with hydroxyl or fluoride groups able to establish multiple supramolecular recognition interactions with SO_2 molecules,[15e,g] and the introduction of basic missing-linker defects and extra-framework barium cations.[15f]

Herein, we take advantage of the already proven high crystallinity and robustness of an oxamato-based 3D MOF with the formula $\mathrm{Ni_2^{II}\{Ni_4^{II}[Cu_2^{II}\text{-}(Me_3mpba)_2]_3\}\cdot 54H_2O}$ (**1**),[17] where $\mathrm{Me_3mpba^{4-}}$ is the *N*,*N*′-2,4,6-trimethyl-1,3-phenylenebis(oxamate) ligand, to perform a post-synthetic solid-state single-crystal to single-crystal (SC to SC) exchange of the nickel(II) cations hosted in the pores of **1** with barium(II) ones to afford a novel heterotrimetallic

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Post-Synthetic Approach Trigger Selective and Reversible Sulphur Dioxide Adsorption on a Metal-Organic Framework

Marta Mon, Estefanía Tiburcio Jesús Ferrando-Soria,* Rodrigo Gil San Millán, Jorge A. R. Navarro,* Donatella Armentano and Emilio Pardo*

pp. 352-364

IV.

Metal-Organic Frameworks for Catalysis

IV.1. Introduction

According to Wilhelm Ostwald, awarded with the Nobel Prize in chemistry in 1909 for his work in catalysis,[1] a catalyst is any substance that has the ability to increase the rate of a chemical reaction, without undergoing any change, and therefore, without being consumed in the process.[2] Hence, the catalysts have become key components in the chemical industry, since they can be used to synthesize large quantities of products at reasonable times and in a more economical and sustainable way.[3]

There are several types of catalysts, but they can be broadly classified in two main groups: homogeneous and heterogeneous.[4,5] In homogeneous catalysis, both the catalyst and the reactants are in a same physical phase, which makes difficult to separate them from the reaction medium and consequently its reuse. However, in heterogeneous catalysis, they are not in the same phase, producing the reaction in an interfacial region. Normally, the reactants are in the gas or solution phase and the catalyst in a solid phase, being possible to separate and reuse it easily. For this reason, heterogeneous catalysts are employed in numerous industrial processes.

As discussed in the introduction, heterogeneous catalysis is an area in which metal-organic frameworks (MOFs) have proven to be very efficient.[6-8] This is due to multiple factors such as its rational design, porous nature, large surface areas, and of course, their crystallinity. The rational design of MOF offers the possibility to create multiple active catalytic sites, either with the choice of the synthetic strategy to construct the MOF, the use of post-synthetic methods (PSMs) or a combination of both of them. Their porous nature allows inserting active species within the pores and, in turn, facilitating the diffusion of reactants from the solution to the active centers. In addition, their crystalline nature makes possible its characterization by X-ray diffraction techniques, allowing a better study of their structure, behavior, as well as mechanistic details of the catalytic reactions.

The catalytic activity of MOFs can be provided by their metal centers (coordinatively unsaturated sites), organic linkers, as well as the species hosted in their pores (metal complexes, nanoparticles, etc.).[9,10] Indeed, the confinement of these active centers can provide very useful chemical environments to carry out certain chemical reactions, as it occurs in enzymes.[11]

Heterogeneous catalysis is a surface phenomenon. Therefore, the performance of catalysts will be better with the more exposed surface area, which increases when the particle size decreases. This fact triggered the use of nanosized metals in catalysis[12] and, hence, the study and development of tools for their characterization (nanoscience), which supposed great advances in the energy and chemical industries.[13] A good example of this is gold. Bulk gold does not show catalytic activity. In contrast, gold nanoparticles catalyze numerous important reactions.[14]

Nanosized metals include nanoparticles (NPs),[15,16] nanoclusters (NCs)[17,18] and single metal atoms.[19,20] NPs have a size between 1 and 100 nm whereas NCs are molecular structures with size less than 1 nm (usually less than 20 atoms) formed by metal-metal bonds, and the single atoms have the smallest size, roughly 0.1 nm. Thus, single-atom catalysts (SACs) are the ones with highest surface/volume ratio and tendency to aggregate, and they are a priori those with the highest catalytic activity if they are stabilized with suitable support materials. However, it should be taken into account that both the shape and chemical composition of the catalyst,[21] as well as the metal-support/reactants interaction are also determining factors.[22] In this sense, despite increasing numbers of reports in this area, there is still a lot of work to be done in order to develop synthetic routes that allow achieving a better control of the size, shape and nuclearity of these nanosized metals species, especially for the case of NCs and single metal atoms.

In particular, ligand-free NCs tend to aggregate, the smaller their size the more they aggregate, due to the lack of blocking protective ligands, which may result in deactivation of the catalyst. However, this can be prevented by using support materials that strongly interacts with the particles, which allows the dispersion and isolation of the active sites from each other, and therefore their stabilization.[23,24] Here is where MOFs come into play, since are promising support materials for nanosized metals,[25-27] offering many advantages in comparison with the traditional supports (zeolites, carbons and aluminosilicates).

There are different strategies to generate MOFs with catalytic activity.[6,9] Among them, we have made use of the already mentioned PSMs (see section III) for the encapsulation or formation of catalytically active species. On the one hand (section IV.A), we have used an anionic MOF to encapsulate Fe^{III} and Ru^{III} species, which has allowed the stabilization of these highly reactive and unstable species in the pores by strong interactions, and therefore, its use in catalysis. This was carried out in two steps from a preformed MOF of formula $Mg^{II}_2\{Mg^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\}\cdot 45H_2O$ [Me_3mpba^{4-} = *N,N'*-2,4,6-trimethyl-1,3-phenylenebis(oxamato)]. Firstly, the transmetallation of the Mg^{II} ions with Ni^{II} ions was performed to obtain a more robust MOF (**Figure IV.1**), which was previously reported by members of the group.[28] Secondly, the Fe^{III} and Ru^{III} species were incorporated by single-crystal to single-crystal (SC to SC) solid-state post-synthetic exchange (PSE) of the nickel atoms hosted in the pores of the MOF.

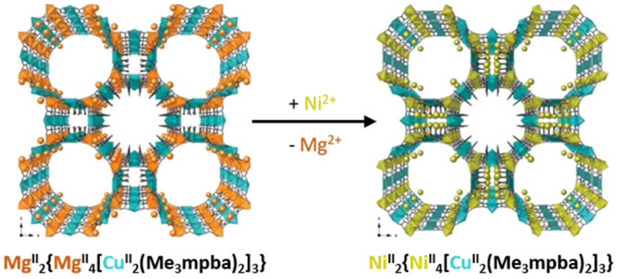

Figure IV.1. Scheme of the transmetallation process and perspective view of 3D anionic networks along the crystallographic *c* axes.

On the other hand (section IV.B), we have used an anionic MOF as template for the synthesis of sub-nanometric metal clusters (sMCs) of application in catalysis. For this, the general strategy utilized has been the functionalization of the pores with the chosen metal salts, and then, the reduction of the metal ions inserted. The fact that metal ions are restricted in number and confined within the MOF channels, provides the possibility of gaining control in the formation of these small metallic species.

In particular, it has been used the anionic MOF, shown in the **Figure IV.1,** for the synthesis of Pd_4 clusters, after three consecutive post-synthetic steps consisting of a transmetallation, a cation exchange and a reduction process. The high robustness and crystallinity of this MOF allowed obtaining highly reactive naked ultrasmall metal entities and, also, the use of SCXRD as the definitive characterization tool for these metal species, never achieved before in MOFs.

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IV.A

Solid-State Incorporation of the Active Species

Article 10.

Isolated Fe(III)-O Sites Catalyze the Hydrogenation of Acetylene in Ethylene Flows under Front-End Industrial Conditions.

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Article

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Isolated Fe(III)−O Sites Catalyze the Hydrogenation of Acetylene in Ethylene Flows under Front-End Industrial Conditions

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Supporting Information

ABSTRACT: The search for simple, earth-abundant, cheap, and nontoxic metal catalysts able to perform industrial hydrogenations is a topic of interest, transversal to many catalytic processes. Here, we show that isolated Fe^{III}−O sites on solids are able to dissociate and chemoselectively transfer H_2 to acetylene in an industrial process. For that, a novel, robust, and highly crystalline metal−organic framework (MOF), embedding Fe^{III}−OH_2 single sites within its pores, was prepared in multigram scale and used as an efficient catalyst for the hydrogenation of 1% acetylene in ethylene streams under front-end conditions. Cutting-edge X-ray crystallography allowed the resolution of the crystal structure and snapshotted the single-atom nature of the catalytic Fe^{III}−O site. Translation of the active site concept to even more robust and inexpensive titania and zirconia supports enabled the industrially relevant hydrogenation of acetylene with similar activity to the Pd-catalyzed process.

INTRODUCTION

Nature uses Fe^{II}-containing hydrogenase enzymes to activate and transfer H_2,[1] and following this concept, chemists have designed organometallic Fe^{II} complexes able to catalyze the hydrogenation of unsaturated carbon bonds in organic molecules.[2] More available and robust forms of Fe, such as Fe^{III} oxides, may also dissociate and transfer H_2 to simpler but industrially relevant substrates, i.e., acetylene, if the catalytic site is suitably designed.[3,4] If so, industrial hydrogenations with convenient Fe^{III} solid catalysts could be carried out.

Polyethylene accounts for nearly 30% of the total production of plastics worldwide, which reaches more than 300 million tons every year. Prior to polymerization, the selective hydrogenation of the remnant acetylene (ca. 1%) in the raw ethylene stream is necessary; otherwise, the polymerization catalyst is poisoned or explosive acetylides can be formed. Traditionally, the hydrogenation of acetylene has been mostly catalyzed by noble metals, including supported noble−metal nanocatalysts, such as Pd, Pt, or Ru.[5] Aiming at reducing the ecological footprint associated with the use of such scarce metals in multiton industrial processes, further efforts are required to develop novel catalysts based on more abundant and less expensive metals such as transition ones.[6−9]

Metal−organic frameworks (MOFs),[10] a highly versatile type of crystalline porous material, have shown excellent results in both gas adsorption[11] and catalysis,[12] which makes them suitable candidates for gas-phase catalysis. MOF catalysis can be originated either from open metal sites[13] of the coordination network, or by taking advantage of the rich host−guest chemistry[14−18] of these porous materials from active guest species judiciously placed in the pores.[19−23] Indeed, MOFs are especially good for supporting metal cations,[23] complexes,[24] or small clusters,[19,25] anchoring them to the walls of their channels. As a result, MOFs can exhibit extremely high catalytic activities, often combined with size-selectivity related to such confined state and exceptional characterization of the guest active species, by means of single crystal X-ray diffraction,[26,27] and also improved reuse capabilities compared to metal catalysts in solution.[19]

The preparation of MOFs has been, traditionally, connected with the use of direct self-assembly methods.[28] However, very recently, a new synthetic avenue has emerged for the fabrication of functional MOFs. This is the so-called postsynthetic (PS) methodology,[29−33] consisting first on the selection of preformed MOFs and second, on the solid-state incorporation[34,35] of the desired functional species within the channels of the MOF.

RESULTS AND DISCUSSION

On this basis, in this work Ni(II) cations hosted in the hydrophilic octagonal pores of a highly crystalline MOF, of

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Isolated Fe(III)–O Sites Catalyze the Hydrogenation of Acetylene in Ethylene Flows under Front–End Industrial Conditions

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Article 11.

Stabilized Ru$[(H_2O)_6]^{3+}$ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope.

ACS Catalysis

Research Article

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Stabilized $Ru[(H_2O)_6]^{3+}$ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope

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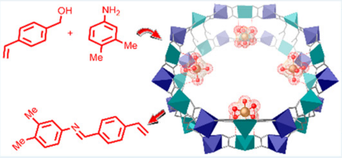
Supporting Information

ABSTRACT: Imines are ubiquitous intermediates in organic synthesis, and the metal−mediated imination of alcohols is one of the most direct and simple methods for their synthesis. However, reported protocols lack compatibility with many other functional groups since basic supports/media, pure oxygen atmospheres, and/or released hydrogen gas are required during reaction. Here we show that, in contrast to previous metal-catalyzed methods, hexa-aqueous Ru(III) catalyzes the imination of primary alcohols with very wide functional group tolerance, at slightly acid pH and under low oxygen atmospheres. The inorganic metal complex can be supported and stabilized, integrally, within either faujasite-type zeolites (Y and X) or a metal organic framework (MOF), to give a reusable heterogeneous catalyst which provides an industrially viable process well below the flammability limit of alcohols and amines.



KEYWORDS: *imine, ruthenium, catalysis, zeolite, metal−organic framework*

Ru is one of the most used and versatile metal catalysts for the dehydrogenation of alcohols,[1] however, it is barely used for the dehydrogenating imination reaction.[2] On one hand, dehydrogenating catalytic Ru(II) complexes (i.e., pincer-type organoRu(II) complexes)[3] produce H_2 during the reaction, which reduces the imine, and on the other hand, high-valent Ru(IV) and (VI) compounds (i.e., tetrapropylammonium perruthenate, TPAP, and RuO_2)[4] and Ru(II) catalysts (i.e., $Ru(PPh)_3Cl_2$ and $Ru(p\text{-cymene})Cl_2$)[5] use sacrificial oxidants to quench the Ru-hydrides, which are not compatible with many functional groups.

Indeed, it is difficult to find functional group tolerant protocols for the imination of alcohols for any metal catalyst.[2a6] The metal catalyst faces the challenge of avoiding hydrogen borrowing mechanisms by rapidly quenching or releasing the so-formed hydrides and, at the same time, shifting the equilibrium toward the imine product. These combined redox/acid−base requirements are even more hampered for aldimines, key intermediates for the synthesis of a plethora of commercially-relevant nitrogen-containing organic molecules,[7] since the dehydrogenation of primary alcohols requires strong basic conditions and promotes decarbonylation reactions.[8] Should any powerful Ru catalyst for the dehydrogenation of alcohols operate in nonbasic media and engage amines without giving hydrogen atoms back or using strong oxidizing conditions, an inherently very active and selective metal catalyst for the direct imination of alcohols will arise.

Table 1 (entries 1−14) shows the imination of 4-vinylbenzyl alcohol (**1**) and 3,4-dimethylaniline (**2**) catalyzed by 5 mol % of 15 representative Ru catalysts, in toluene at 90 °C, and with 2 equiv of O_2, which corresponds to the amount of air in the vial. Notice that these atmospheric conditions are extremely mild and fulfill flammability limitations in industry for organic compounds. The first results in Table 1 confirm the difficulties mentioned above, and Ru(II) or (III), salts and complexes (entries 1−5), pincer-type complexes (entries 7−10), and supported Ru nanoparticles (entries 11−12) do not give imine **3** (complex A Milstein's aceptorless dehydrogenating catalyst gives 35% of the amine product, entry 6),[2c] while high-valent Ru compounds (entries 13−14) act as stoichiometric rather than catalytic agents, to yield the amount of imine **3** corresponding to reducible Ru.

In contrast, $[Ru(H_2O)_6]^{3+}$ (entry 15) shows truly catalytic activity and achieves 21% of imine **3**. This Ru species, prepared in HBF_4 solutions in the 60s[9] and later supported in faujasite-type zeolites by simple cation exchange,[10] has rarely been reported for catalysis,[11] despite its simplicity. The combination of acidity, accessibility, and water-compatibility in a same Ru site seems favorable for the imination of alcohols. Unfortunately, monitoring the homogeneous reaction by in-situ

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Supporting Information.

Stabilized Ru[(H$_2$O)$_6$]$^{3+}$ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope

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IV.B

Synthesis of Sub-Nanometric Metal Clusters and Single Metal Atoms

Article 12.

The MOF-Driven Synthesis of Supported Palladium Clusters with Catalytic Activity for Carbene-Mediated Chemistry.

nature materials

ARTICLES

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The MOF-driven synthesis of supported palladium clusters with catalytic activity for carbene-mediated chemistry

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The development of catalysts able to assist industrially important chemical processes is a topic of high importance. In view of the catalytic capabilities of small metal clusters, research efforts are being focused on the synthesis of novel catalysts bearing such active sites. Here we report a heterogeneous catalyst consisting of Pd_4 clusters with mixed-valence 0/+1 oxidation states, stabilized and homogeneously organized within the walls of a metal–organic framework (MOF). The resulting solid catalyst outperforms state-of-the-art metal catalysts in carbene-mediated reactions of diazoacetates, with high yields (>90%) and turnover numbers (up to 100,000). In addition, the MOF-supported Pd_4 clusters retain their catalytic activity in repeated batch and flow reactions (>20 cycles). Our findings demonstrate how this synthetic approach may now instruct the future design of heterogeneous catalysts with advantageous reaction capabilities for other important processes.

Ultrasmall metal clusters[1–5] have attracted a great deal of interest as extremely active and selective catalysts for organic reactions[6,7]. Despite the efforts made, there is yet more work to be done to fully understand the exact nature of the catalytic species, their reactivity, structure, shape and nuclearity[8,9]. Ligand stabilization[10] and matrix-supported[11,12] are the most efficient strategies to synthesize and characterize metal clusters. While the former allows structure determination of the cluster metal complex by single-crystal X-ray crystallography, these compounds rarely find applications in catalysis[13] since ligand exchange with the reactants triggers decomposition of the cluster. In clear contrast, clusters supported on solids are stable catalytic species with highly reactive uncoordinated atoms[1], but only nuclearity and oxidation state of the metal by X-ray absorption spectroscopies combined with high-resolution microscopies can be addressed. Thus, the synthesis of supported metal clusters with precise topological and electronic properties, as occurs in metal complexes, would be of much interest.

In this context, metal–organic frameworks (MOFs)[14] have emerged[15] as very versatile materials for encapsulating catalytic nanosized species within their channels[16]. In addition, the regular and well-defined channels in MOFs appear, theoretically, as the perfect hosts to obtain information about the nature of the metallic catalyst species by means of single-crystal X-ray crystallography. However, after a number of studies on this topic showing small 1–2 nm metal nanoparticles[17–20], it is difficult to find reports of metal clusters below the nanometre size within MOF matrices.

Metal carbenoids are powerful catalytic and synthetic intermediates in organic synthesis, and different metals have been reported to form and transfer carbenes[21]. Despite Pd compounds being found as catalysts for a plethora of fundamental transformations in organic synthesis, such as hydrogenations, carbon–carbon couplings, and many others[22], they have been only occasionally employed as catalysts in carbene-transfer processes[23–27].

Here we report the preparation of $Pd_4^{0/1+}$ clusters stabilized by the anionic framework of a MOF. The material is able to catalyse representative carbene-mediated reactions such as the inter- and intramolecular Buchner ring expansion reaction, the alcohol insertion and the dimerization of diazocompounds, to give some unique naturally occurring and synthetically useful products[28–30]. This new catalytic behaviour of Pd emerges due to the stabilization of intermediate Pd^+ valence within the supported-MOF cluster, which enables carbene bonding to give a catalytic activity that exceeds by one order of magnitude that of the state-of-the-art catalysts for these reactions. In addition, the solid catalyst can be recovered and reused up to 20 times in batch without any reactivation treatment or depletion of the catalytic activity, or operated in flow with solvent recycling during hours.

Synthesis and characterization of Pd_4-MOF

Herein, we take advantage of the emerging post-synthetic methods[31,32] to synthesize (see Methods), in three steps, $[Pd_4]^{2+}$ clusters from a preformed highly porous anionic MOF of formula $Mg_2^{II}\{Mg_4^{II}[Cu_2^{II}(Me_3mpba)_2]_3\}\cdot 45H_2O$ (**1**) [Me_3mpba^{4-} = *N,N′*-2,4,6-trimethyl-1,3-phenylenebis(oxamate)] (Fig. 1a) by: the already reported transmetallation[32] of **1** to yield the more robust MOF $Ni_2^{II}\{Ni_4^{II}[Cu_2^{II}(Me_3mpba)_2]_3\}\cdot 54H_2O$ (**2**) (Fig. 1b); the

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nature materials

SUPPLEMENTARY INFORMATION

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The MOF–driven synthesis of supported palladium clusters with catalytic activity for carbene–mediated chemistry

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V.

Conclusions and Perspectives

This PhD thesis reports the rational design and development of novel metal-organic frameworks (MOFs) with applications in different technological areas of interest. Through the different results obtained, we have proven the great versatility of these materials, as well as the viability of the proposed synthetic strategies.

Six oxamidato-based MOFs have been synthesized from different amino acids derivatives (*L*-methionine, *L*-serine, *L*-threonine and *L*-histidine methyl ester), utilizing the "complex-as-ligand" approach. The use of these biomolecules allowed us to obtain a family of MOFs that are chiral, biocompatible, stable in water and present functional pores of different size, shape and reactivity. These features have made them good platforms in a wide range of applications.

In particular, the MOFs derived from the amino acid *L*-methionine have pores decorated with very flexible and accessible thioether groups, allowing to capture gold or mercury species from aqueous media, in a selective and efficient manner, as shown in section II. On the other hand, MOFs derived from *L*-serine and *L*-threonine possess pores decorated with hydroxyl groups, capable of capturing different organic molecules such as dyes or drugs, as well as discriminating and separating lanthanide salts, due to its ability to establish specific host-guest interactions.

The high crystallinity and robustness of the synthesized materials have made possible to unveil the structures by single-crystal X-ray diffraction (SCXRD), giving unprecedented snapshots of the host-guest interactions, which is of main relevance to design even more performant MOF adsorbents. In addition, these MOFs are environmentally friendly, cheap and easy-to-prepare in large-scale. Furthermore, they have been shown to be reusable adsorbents, which makes them very attractive from an environmental and industrial point of view.

Another strategy that has allowed us to design MOFs for specific applications is the use of post-synthetic methods (PSMs), such as metal substitution (transmetallation) or the exchange of molecules hosted in the pores. These methodologies offer the possibility to improve or incorporate new properties in materials without altering its structure, as shown in section III and IV.

In particular, in section III, through the exchange of molecules hosted in the pores of the MOF derived from the amino acid *L*-histidine, a ferroelectric material has been obtained, which have great interest for its important applications in data storage, sensing and energy harvesting. In addition, it has been prepared a material capable of adsorbing SO_2, in a reversible way, by exchange of the ions hosted in the pores of an oxamato-based MOF. This has allowed to obtain a new material that could carry out the desulfurization of the gases generated in the fossil fuels combustion, in an economic and sustainable way.

In section IV, post-synthetic modifications have been used, in particular, to obtain MOFs with catalytic activity. We have employed an anionic oxamato-based MOF to encapsulate highly reactive and unstable cationic species in the pores. In this way, two materials that are very efficient as heterogeneous catalysts have been prepared, allowing to carry out important reactions at the industrial level (section IV.A). Finally, we have used the same anionic oxamato-based MOF as template for the *in-situ* synthesis of sub-nanometric metal clusters. Thus, we have developed a very effective strategy to synthesize nanosized metals, which have great catalytic activity (section IV.B). In contrast to other methods commonly used, the presented strategy allows having a fine control in the formation of these small metallic species, thanks to the fact that the metal ions are restricted in number and confined within the pores.

Future plans derived from the results of these works are:

- The preparation of suitable devices for the practical application of the materials, such as membranes, pellets, films, among others, with the presented MOFs.

- The synthesis of new MOFs that allow the elimination, efficient and in one-step, of inorganic and organic pollutants of aquatic ecosystems. For this, the strategy to be used would be to obtain multivariate-MOFs (MTV-MOFs), which are materials that contain two (or more) different ligands. In particular, a good starting point will be to utilize two different amino acids, such as *L*-methionine and *L*-serine. This approach will allow obtaining MOFs with pores decorated by several amino acid residues.

- The use of the pores of MOFs as nanoreactors, but in this case, for the *in-situ* synthesis and physical characterization of functional supramolecular metallacyclic complexes (SMCs), otherwise hardly accessible, within their large pores. For this, in first a stage the insertion of metal ions within the channels of an anionic MOF will be carried out, and then, an organic ligand with appealing encoded coordination information will be incorporated to build up the SMCs within MOFs channels.