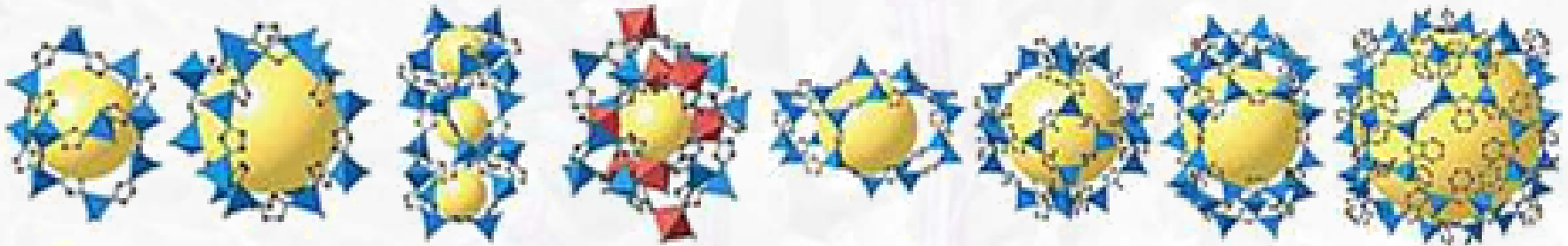


MOFs porosos: “tallando” el espacio en arquitecturas supramoleculares

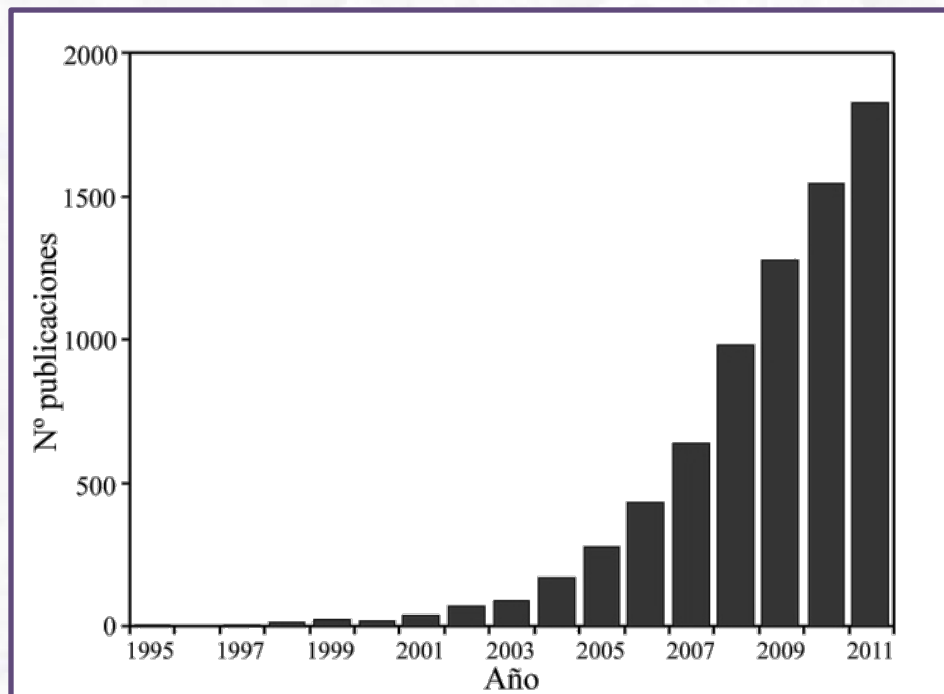


**Ainhoa Calderón¹, Arkaitz Fidalgo¹, Francisco Llano¹, Begoña Bazán¹,
Gotzone Barandika², Karmele Urtiaga¹, María Isabel Arriortua^{1*}**

1. Dpto. de Mineralogía y Petrología. UPV/EHU, Fac. Ciencia y Tecnología. Leioa (Bizkaia)

2. Dpto. de Química Inorgánica. UPV/EHU, Fac. Farmacia. Vitoria-Gasteiz (Araba)

MOF (Metal Organic Framework) → O. M. Yagui 1995



- Versatilidad en su diseño
- Estructuras abiertas → *host-guest chemistry*
- Flexibilidad → *transformaciones estructurales*

Yaghi O. M., Li G. M., Li H. L., *Nature*, **378**, 703-706, 1995.

Yaghi O. M., Li H. L., *J. Am. Chem. Soc.*, **117**, 10401-10402, 1995.

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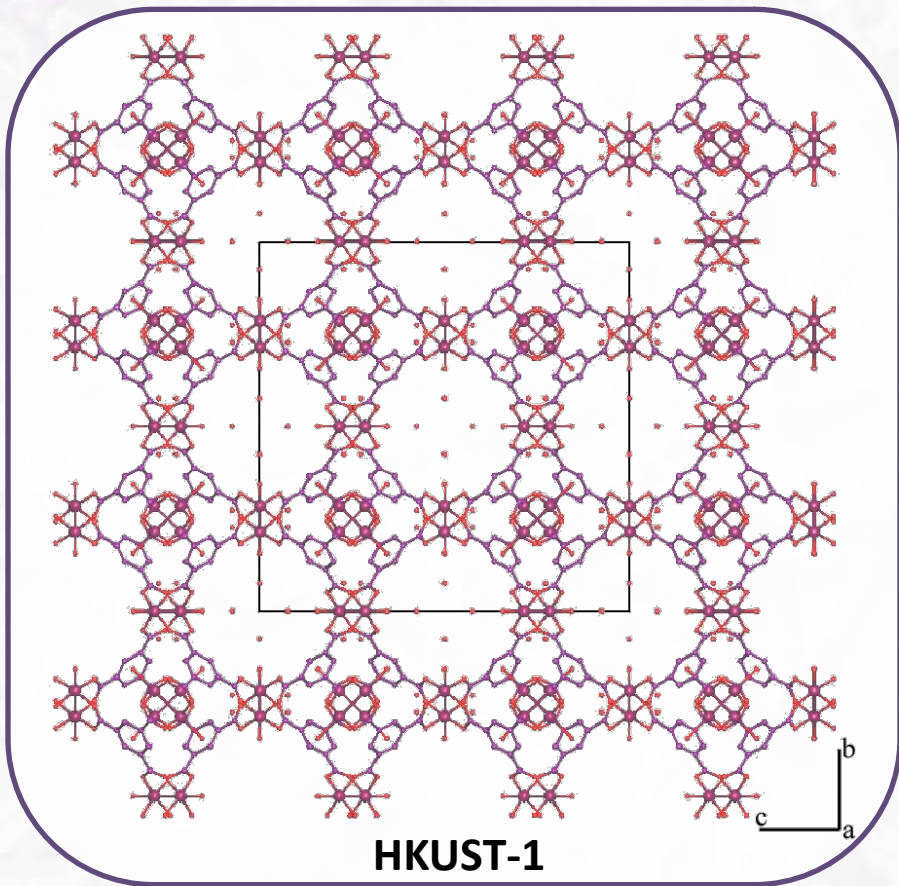
eman ta zabal zazu



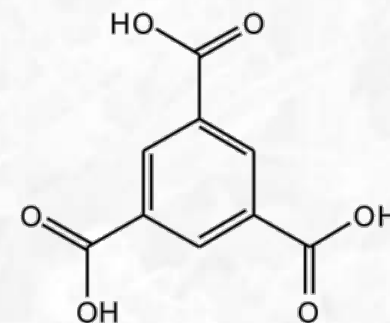
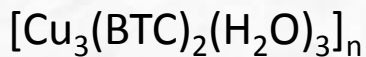
B. Bazán

MOFs porosos basados en ligandos policarboxílicos

1^{er} MOF 3D



HKUST-1



H₃BTC: ác. benceno-1,3,5-tricarboxílico

Estable hasta 240°C
9 Å x 9 Å

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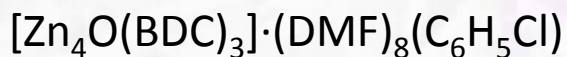
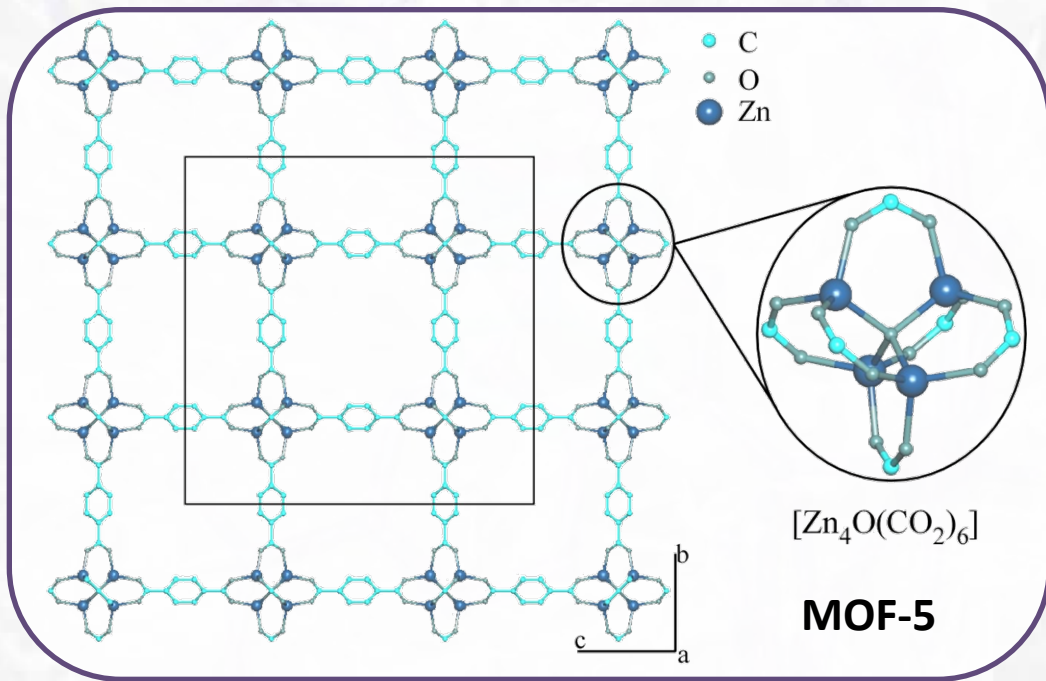
eman ta zabal zazu



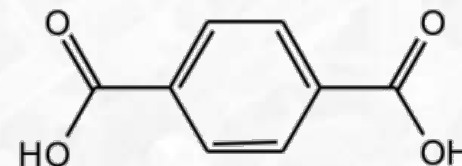
B. Bazán

MOFs porosos basados en ligandos policarboxílicos

O. M. Yaghi



H₂BDC: ácido benceno-1,4-dicarboxílico



Estable hasta 300°C
Elevada área superficial

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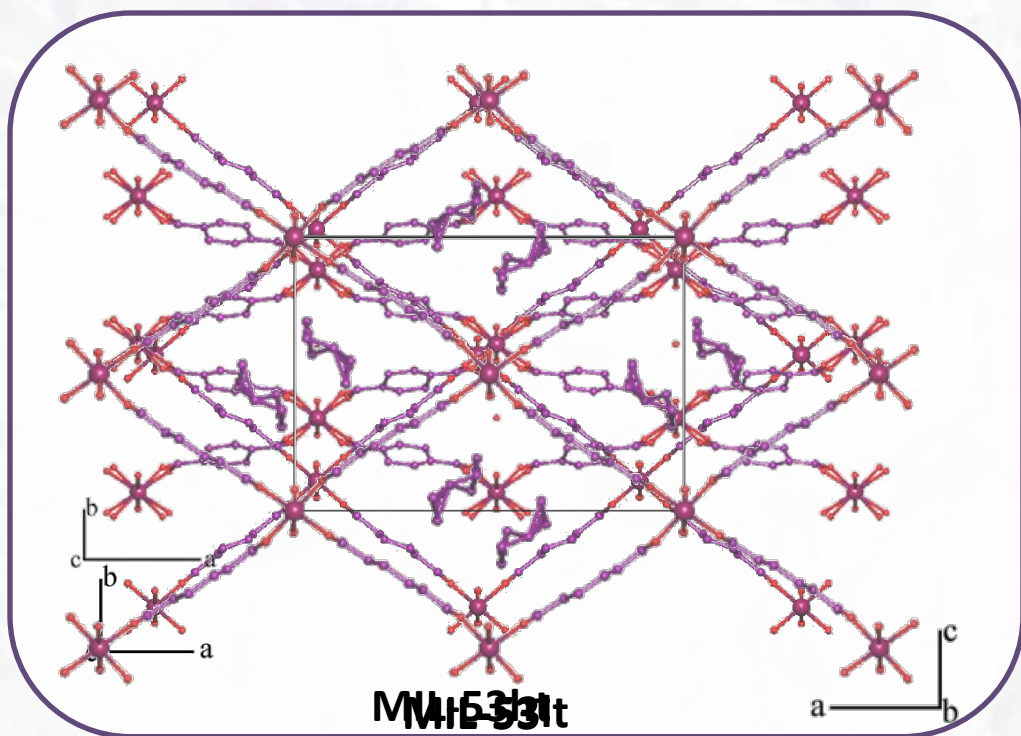
B. Bazán

Introducción

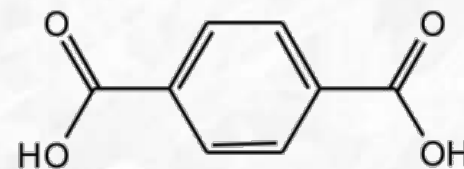
MOFs porosos basados en ligandos policarboxílicos

G. Férey

(Materials Institute Lavoisier)



MOF-5



H₂BDC: ácido benceno-1,4-dicarboxílico

Estable hasta 250°C
Mantiene la porosidad

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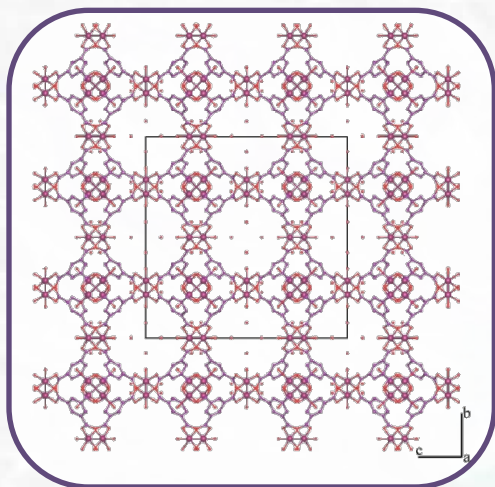


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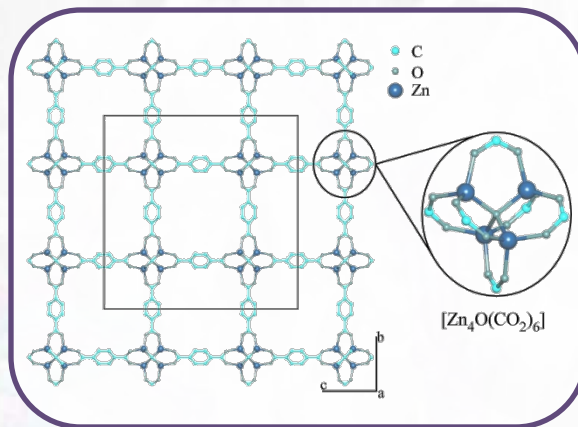


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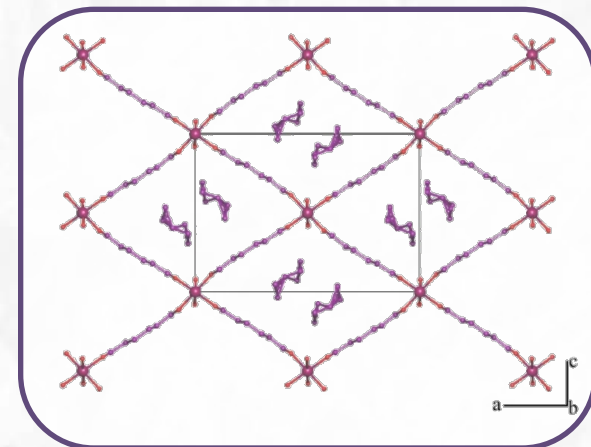
Introducción



HKUST-1
 $[Cu_3(BTC)_2(H_2O)_3]_n$



MOF-5
 $[Zn_4O(BDC)_3] \cdot (DMF)_8(C_6H_5Cl)$



MIL-53
 $[Cr(OH)(BDC)] \cdot (H_2BDC)_{0.75}$

POROSIDAD → HOST-GUEST CHEMISTRY

POROSIDAD → APLICACIONES

MOFs

- Separación de gases
- Almacenamiento de gases
- Intercambio iónico
- Catálisis
- Liberación de fármacos
- Conductividad
- Sensor

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TRAYECTORIA DEL GRUPO DE INVESTIGACIÓN

Compuestos de coordinación extendidos (CCE)
Clúster y polímeros 1D, 2D, 3D



propiedades magnéticas en
compuestos de dimensionalidad
creciente

Híbridos Inorgánico-Orgánicos (HIO)
Estructuras 1D, 2D, 3D



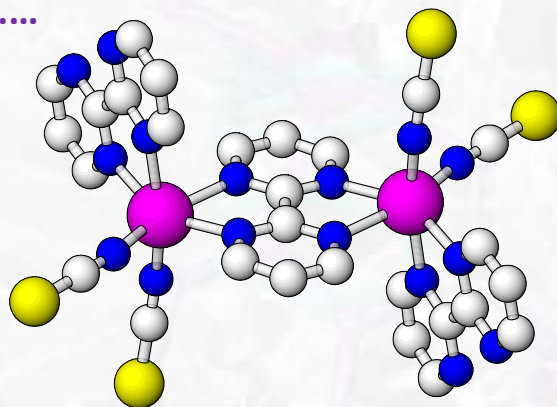
estructuras abiertas en
compuestos con plantillas
orgánicas

MOF (Metal Organic Framework)

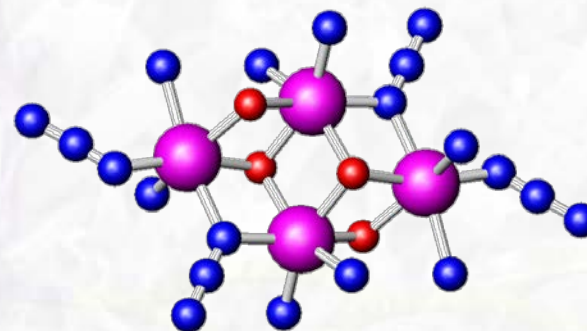


clústers ← monómeros

dímeros
trímeros
tetrámeros
.....



dímero
 $[Mn_2(NCS)_4(bipym)_3]$



tetrámero
 $[M_2(X)_2(dpk·OR)_2]_2$



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Cortés, R.; Urriaga, M.K.; Lezama, L.; Pizarro, J.L.; Arriortua, M.I. y Rojo, T. *Inorg. Chem.*, **36**, 5016, **1997**.
 Serna, Z.E.; Barandika, M.G.; Cortés, R.; Urriaga, M.K.; Barberis, G.E. y Rojo, T. *J. Chem. Soc., Dalton Trans.*, **29**, **2000**.
 Serna, Z.E.; Lezama, L.; Urriaga, M.K.; Arriortua, M.I.; Barandika, M.G.; Cortés, R. y Rojo, T. *Angew. Chem. Int. Ed.*, **39**, 344, **2000**.

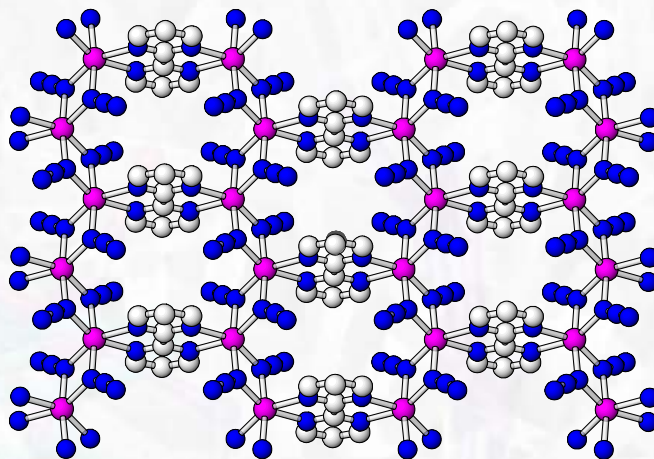
monómeros

clústers

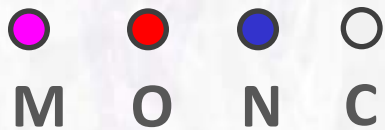
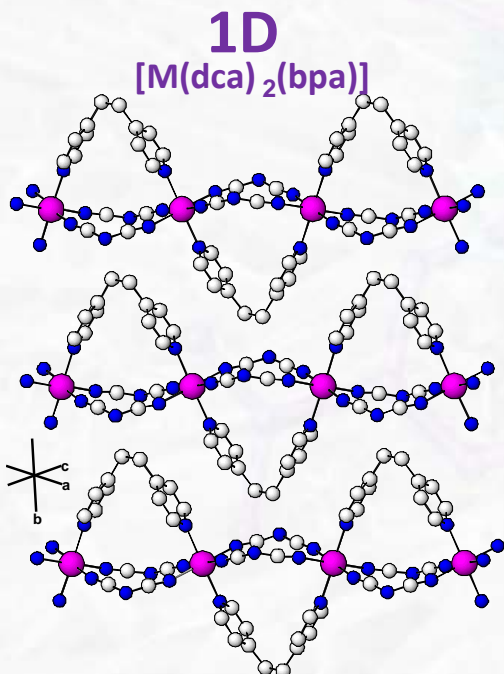
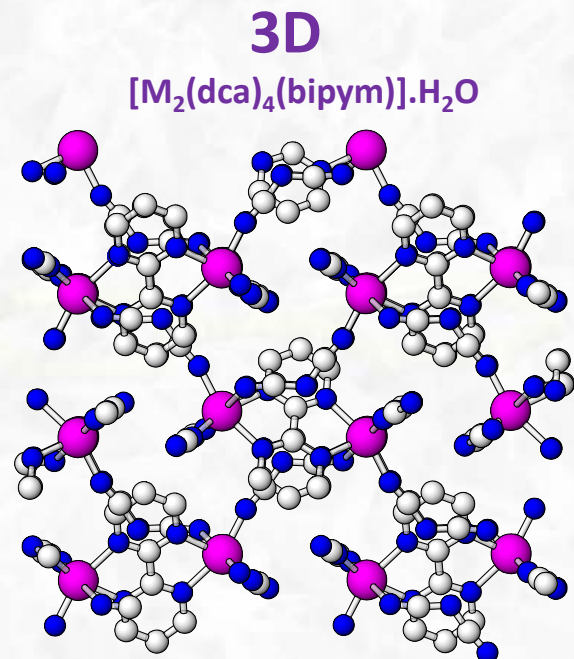
dímeros
trímeros
tetrámeros
.....

polímeros

1D
2D
3D



2D
 $[Mn_2(N_3)_4(bipy)]_n$



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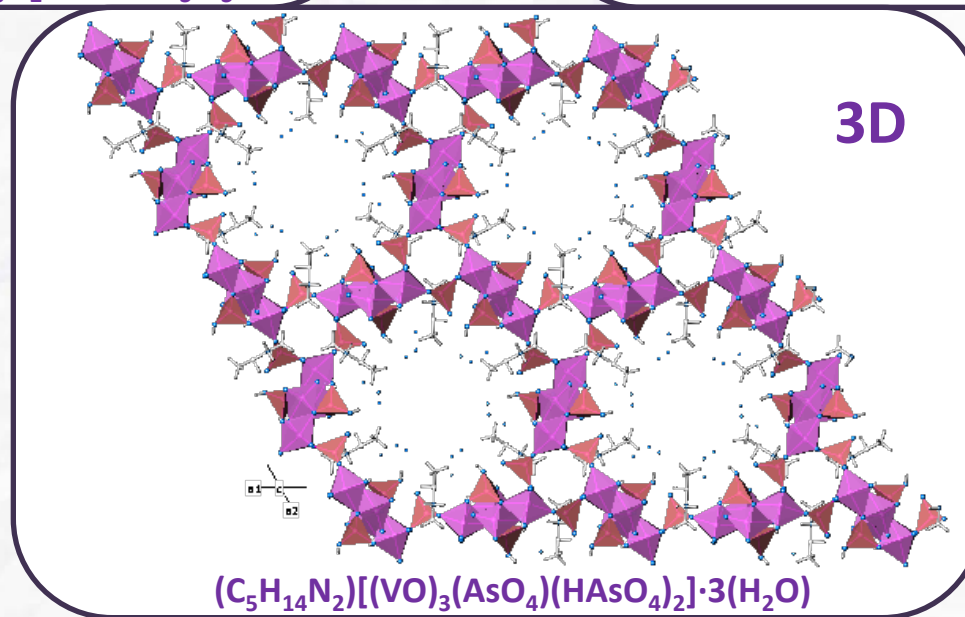
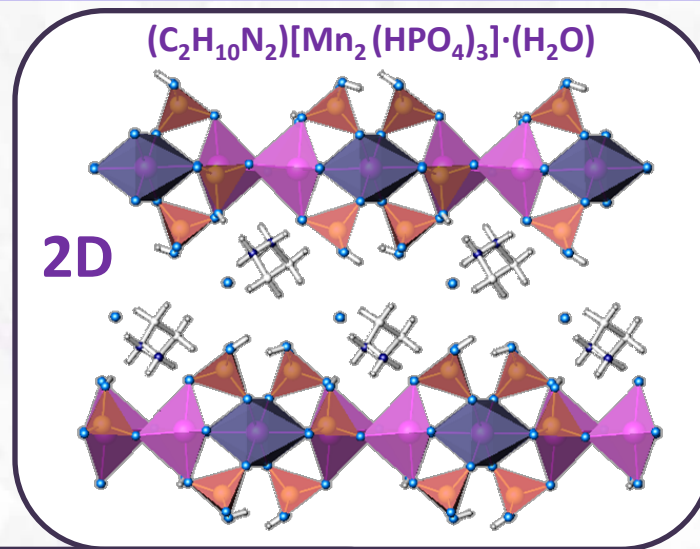
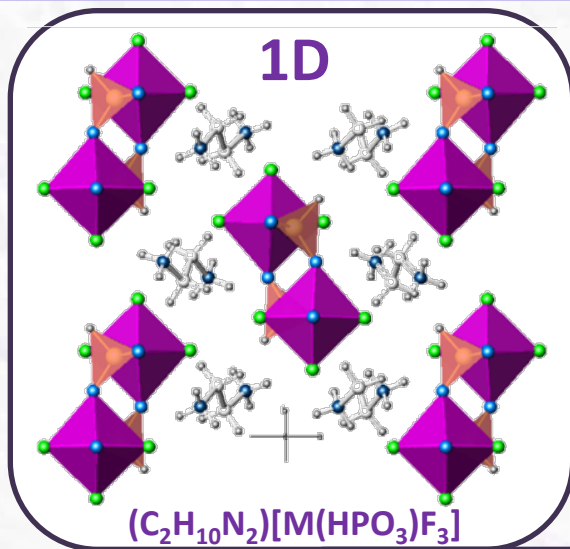
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Martín, S.; Barandika, M.G.; Larramendi, J.I.R.; Cortés, R.; Font-Bardia, M.; Lezama, L.; Serna, Z.E.; Solans, X. y Rojo, T. *Inorg. Chem.*, **40**, 3687, **2001**; Hernández, M.L.; Urriaga, M.K.; Barandika, M.G.; Cortés, R.; Lezama, L.; De la Pinta, N.; Arriortua, M.I. y Rojo T. *J. Chem. Soc., Dalton Trans.*, 3010, **2001**.



S. Fernández, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo, *Angew. Chem. Int. Ed.*, **41**, 3683-3685, **2002**.

J. Escobal, J.L. Pizarro, J.L. Mesa, R. Olazcuaga, M.I. Arriortua, T. Rojo, *Chem. Mater*, **12**, 376-382., **2000**.

T. Berrocal, J.L. Mesa, J.L. Pizarro, B. Bazán, M. Iglesias, M.I. Arriortua, T. Rojo, *Chem. Commun.*, 4738-4740, **2008**.

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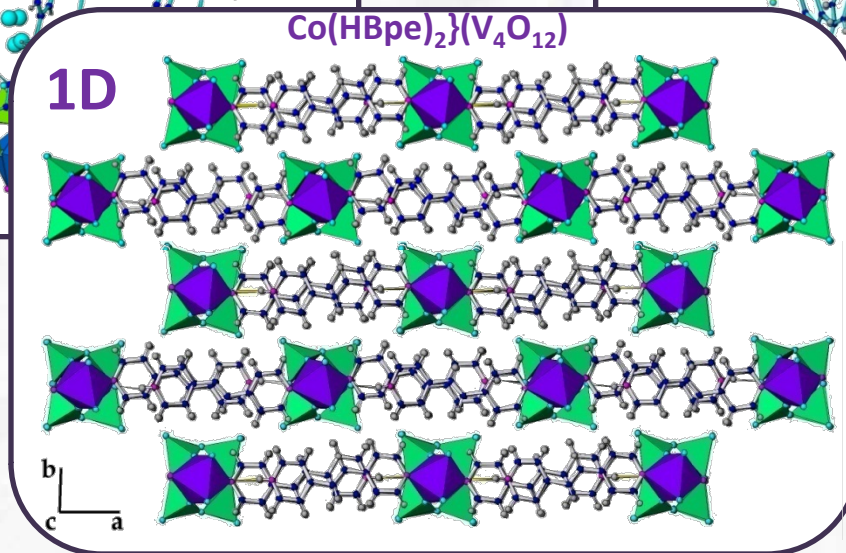
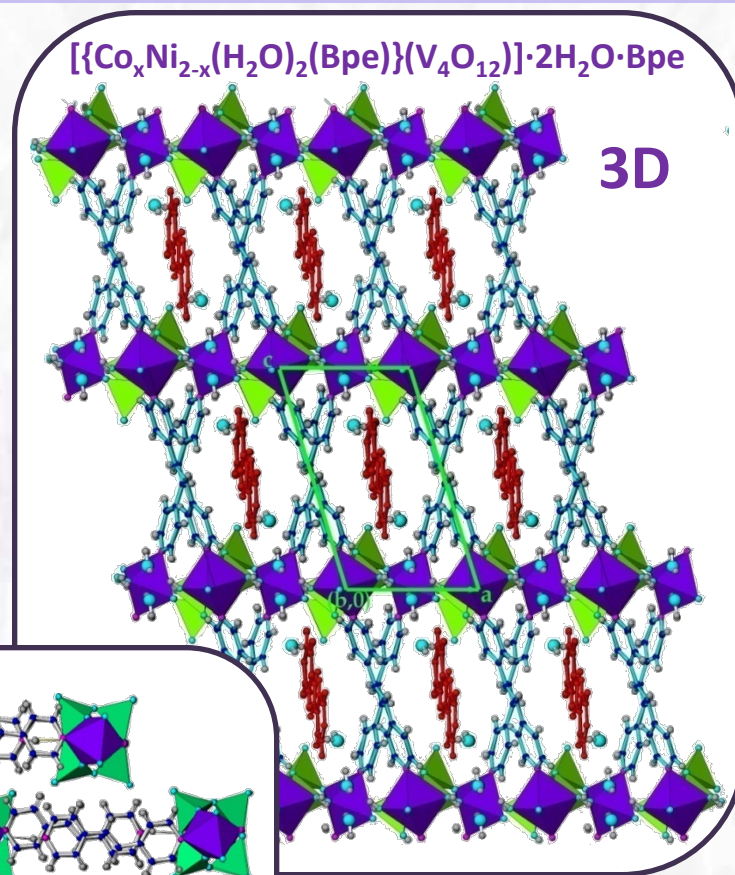
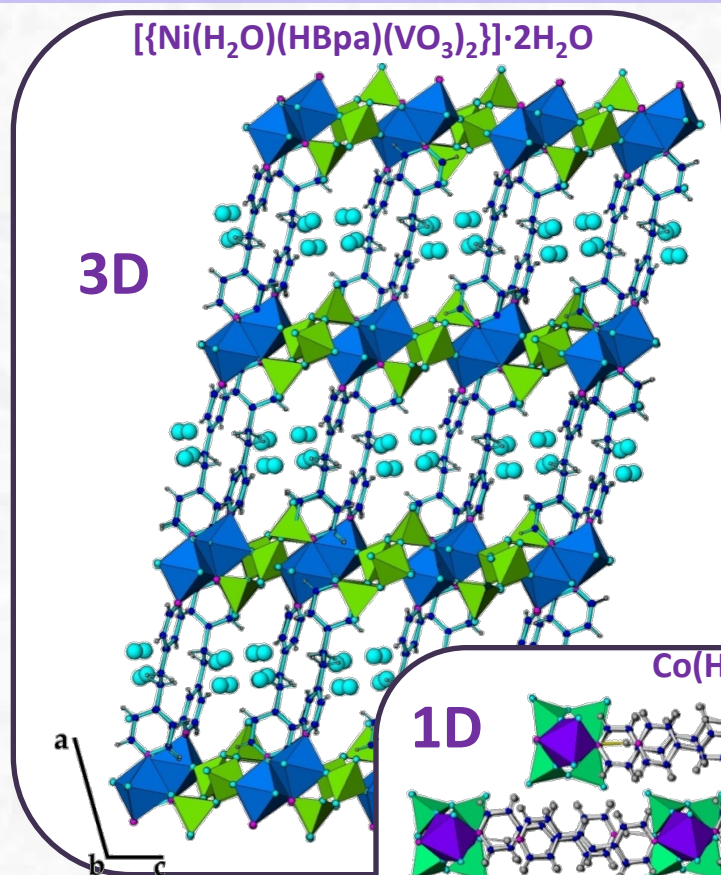
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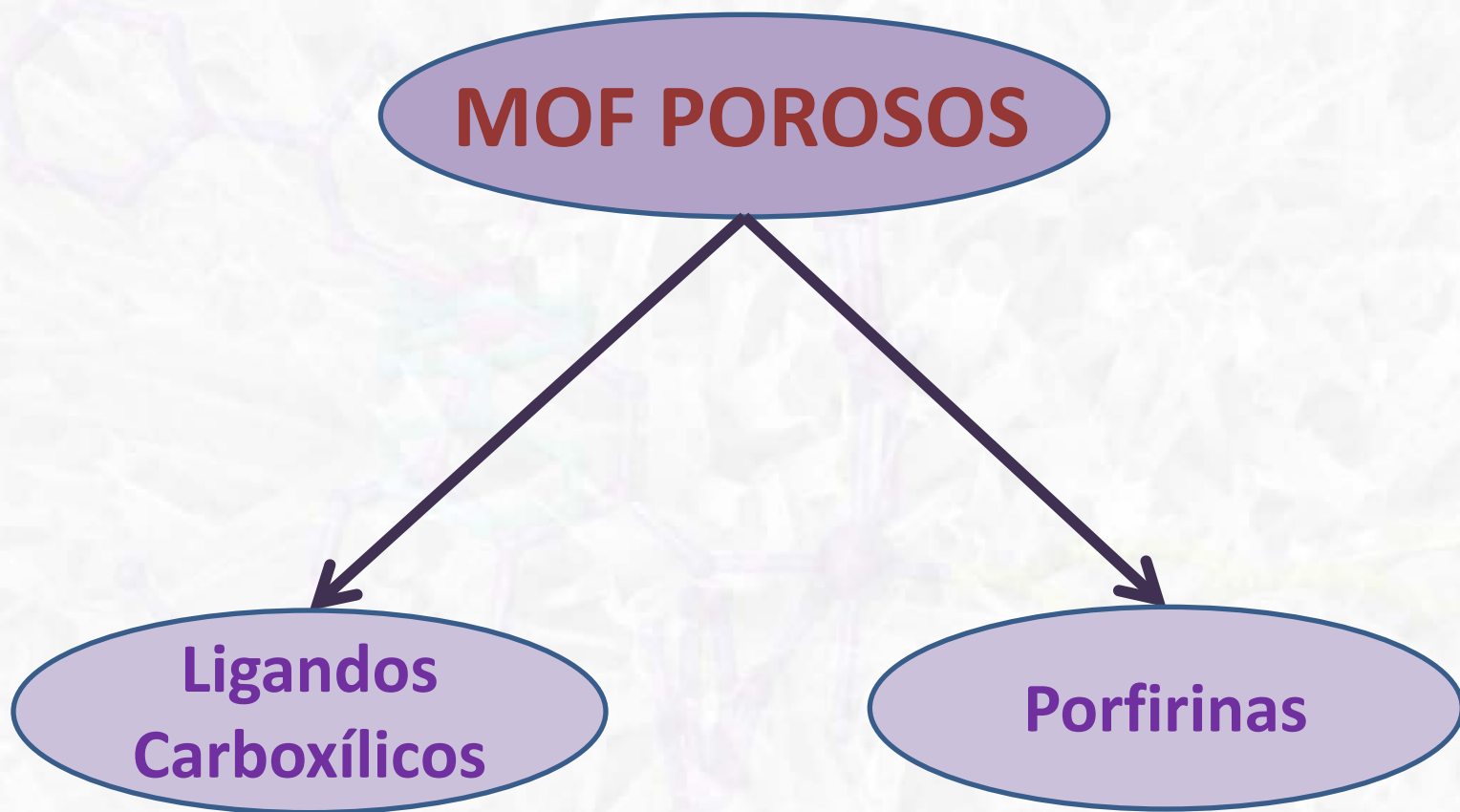
Introducción

HIO-Vanadatos



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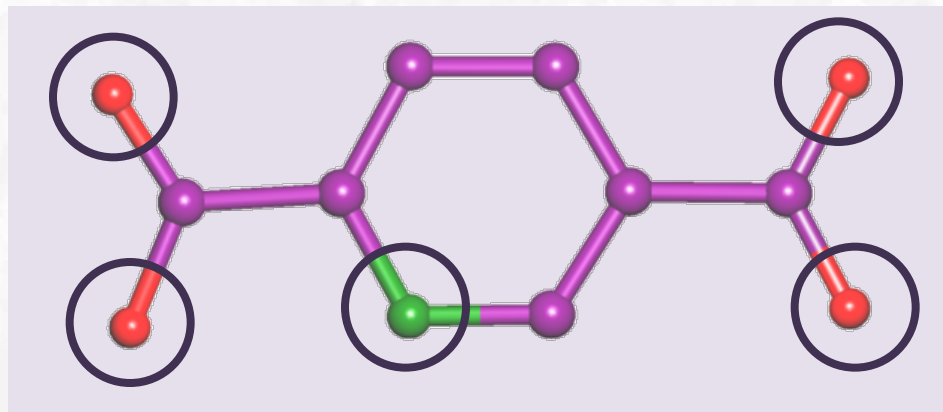
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piridin-2,5-dicarboxilato PDC

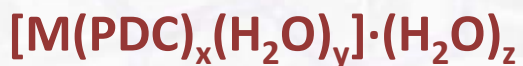
Rigidez estructural Libertad conformacional



Adaptabilidad estructural



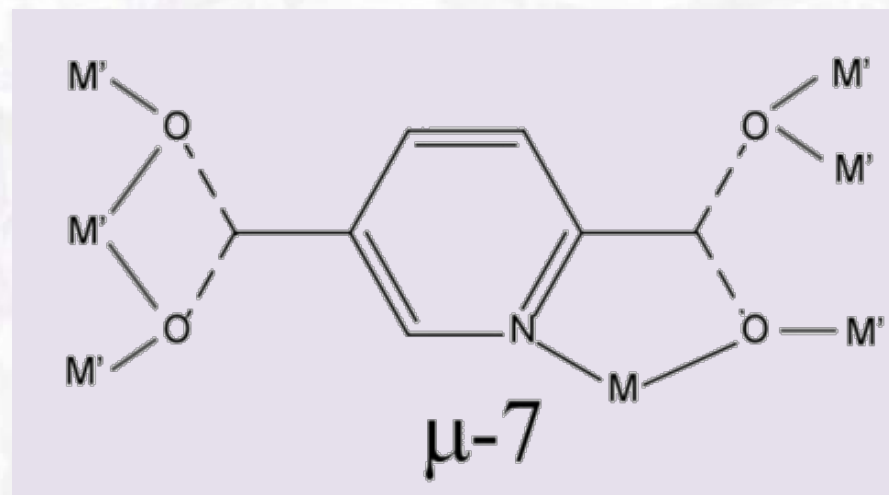
52 estructuras diferentes



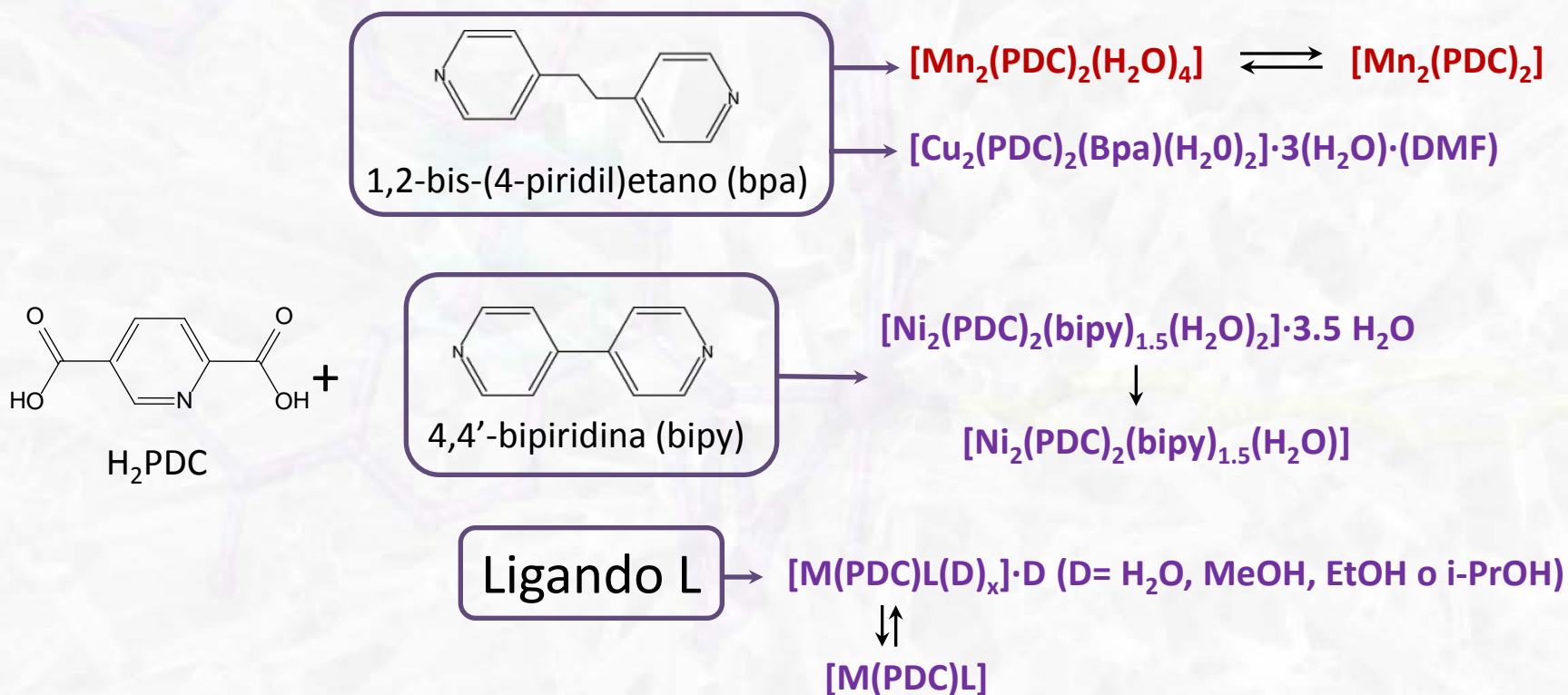
Versatilidad en la coordinación



21 modos de coordinación



Combinación de ligandos O-dadores y N-dadores (extensión y robustez)



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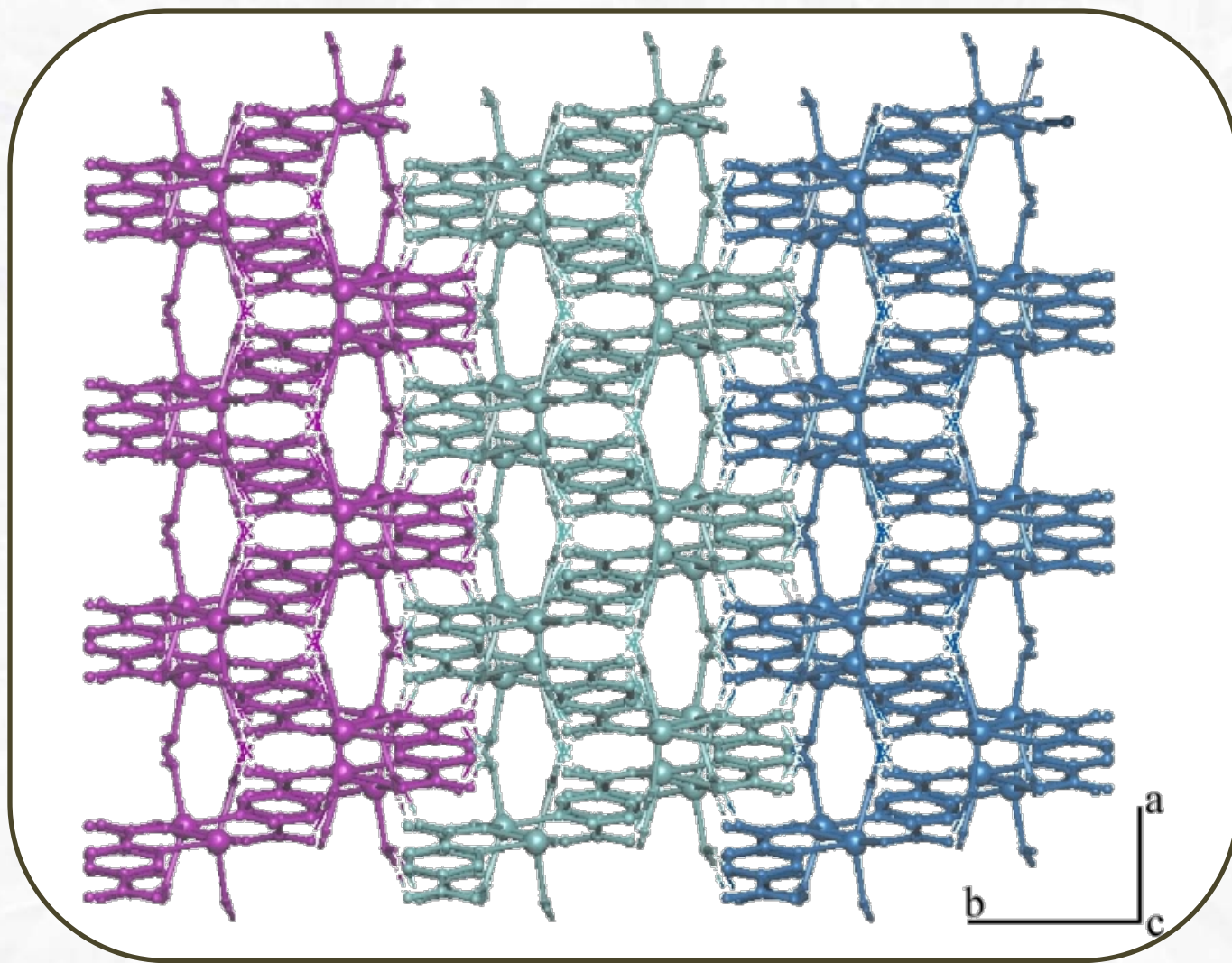


Solicitud de patente nº ID02335677.

Arriortua M. I., Barandika M. G., Bazán B., Calderón-Casado A. y M. K. Urriaga (UPV/EHU), 2011.



Estructura Cristalina



Entramado 3D supramolecular

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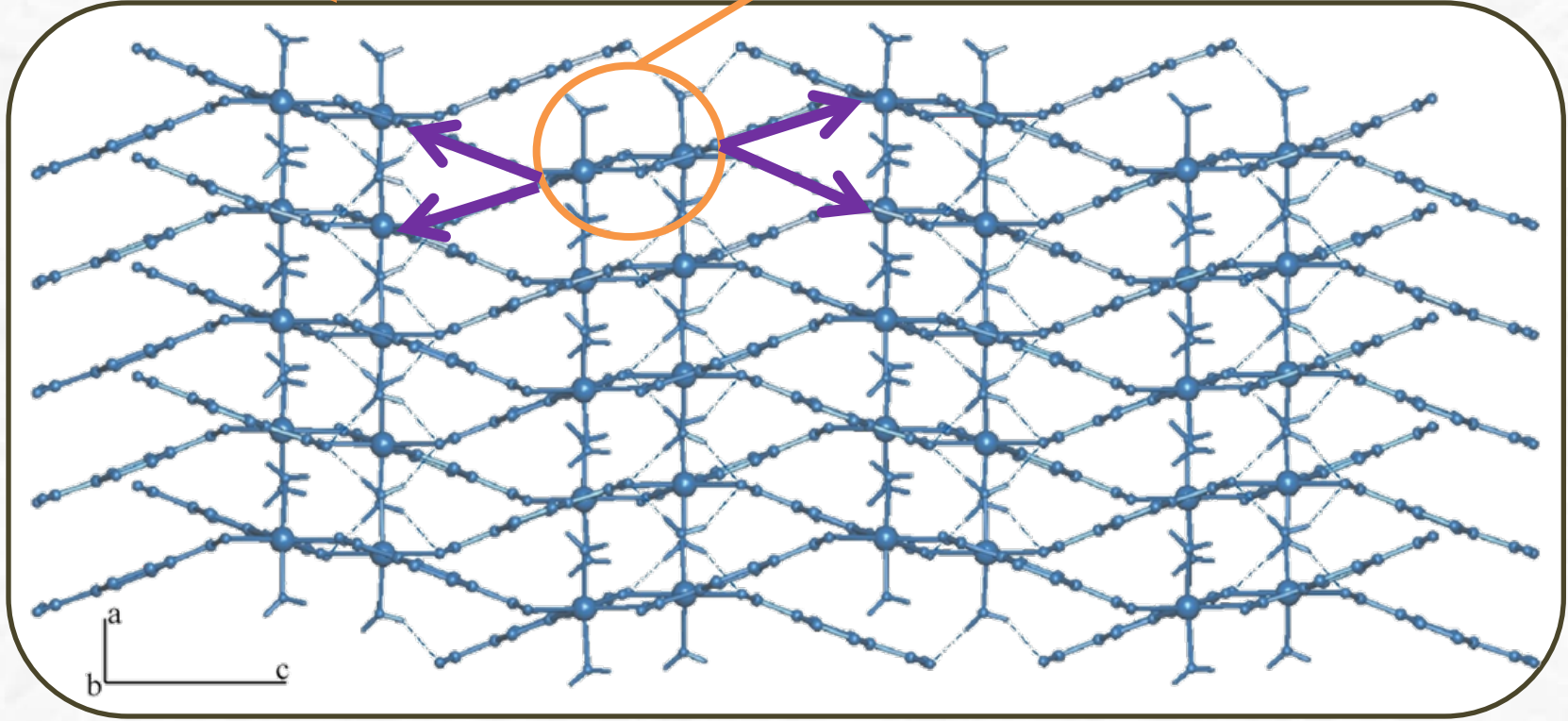
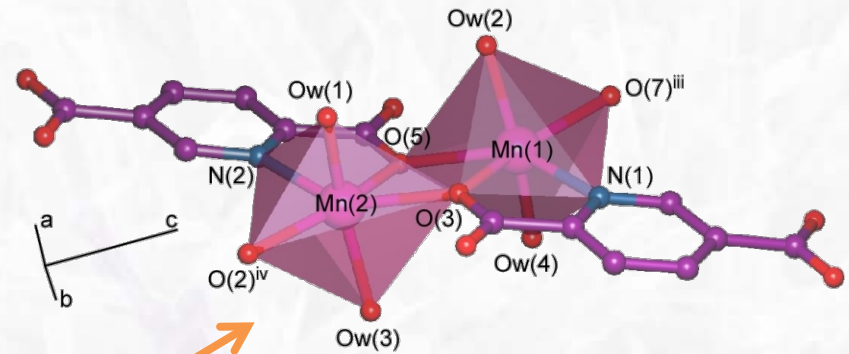
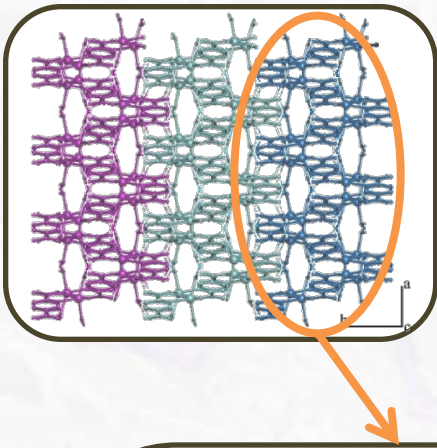
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Estructura Cristalina



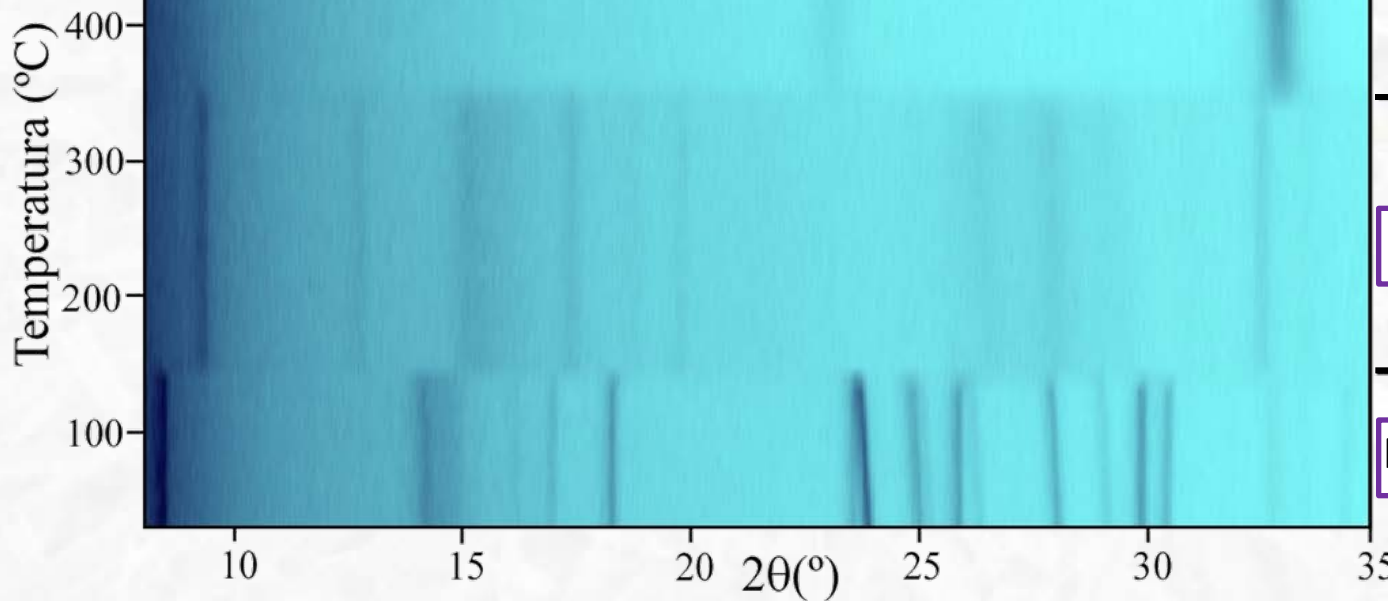
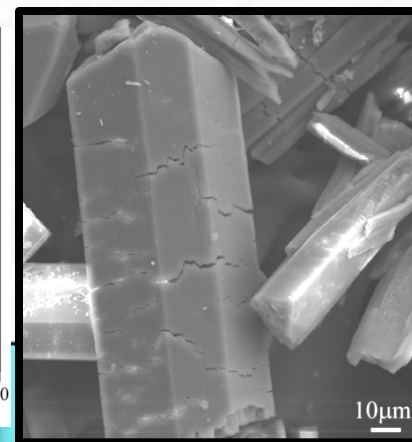
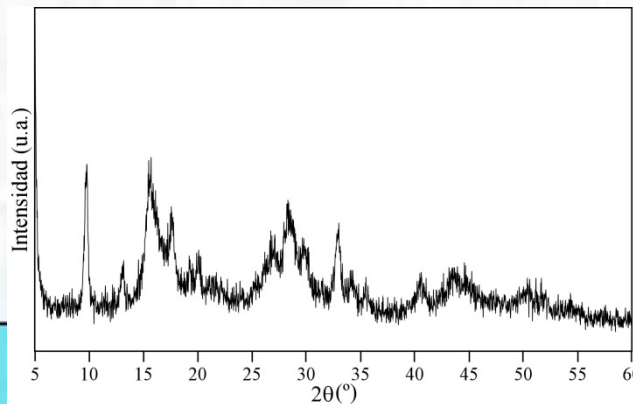
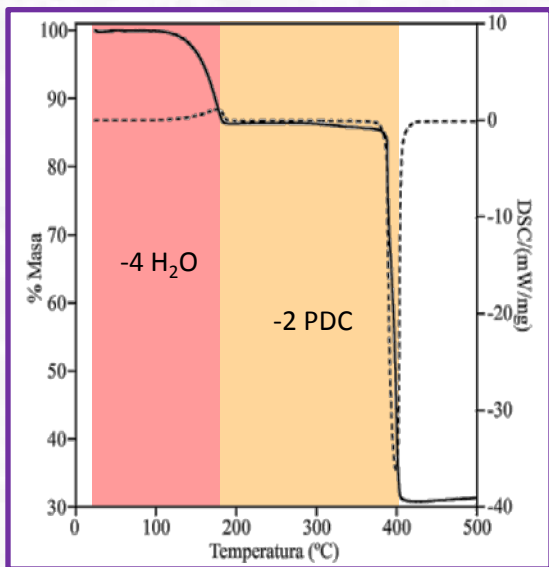
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Transformación estructural



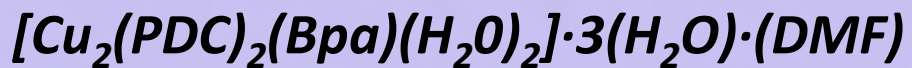
→ 360°-370°

Fase anhidra

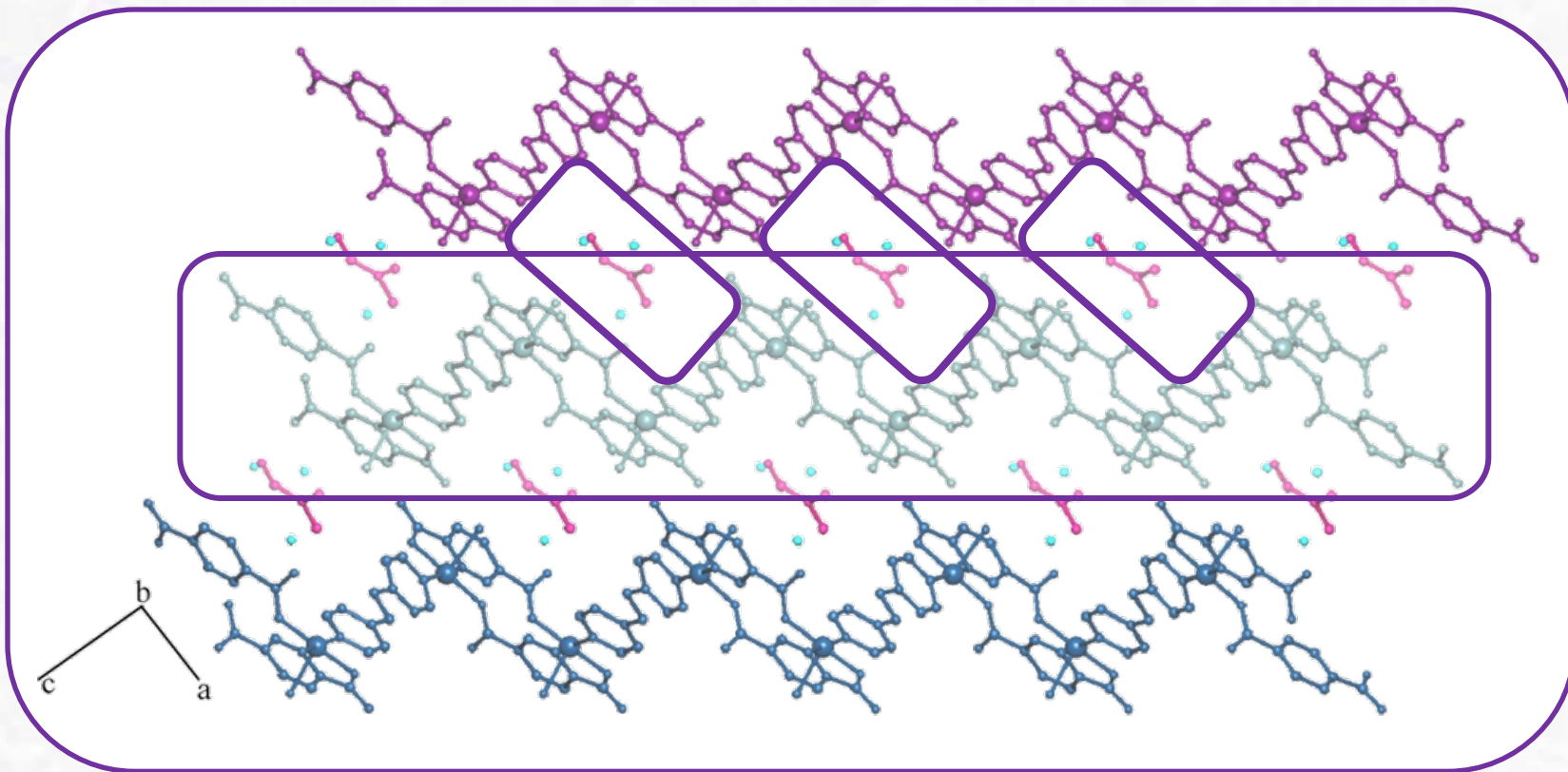
→ 140°-150°

$Mn_2(PDC)_2(H_2O)_4$





Estructura Cristalina



Entramado 3D supramolecular

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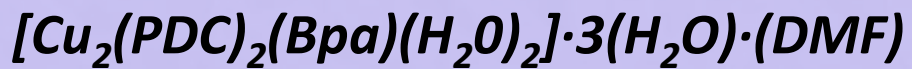


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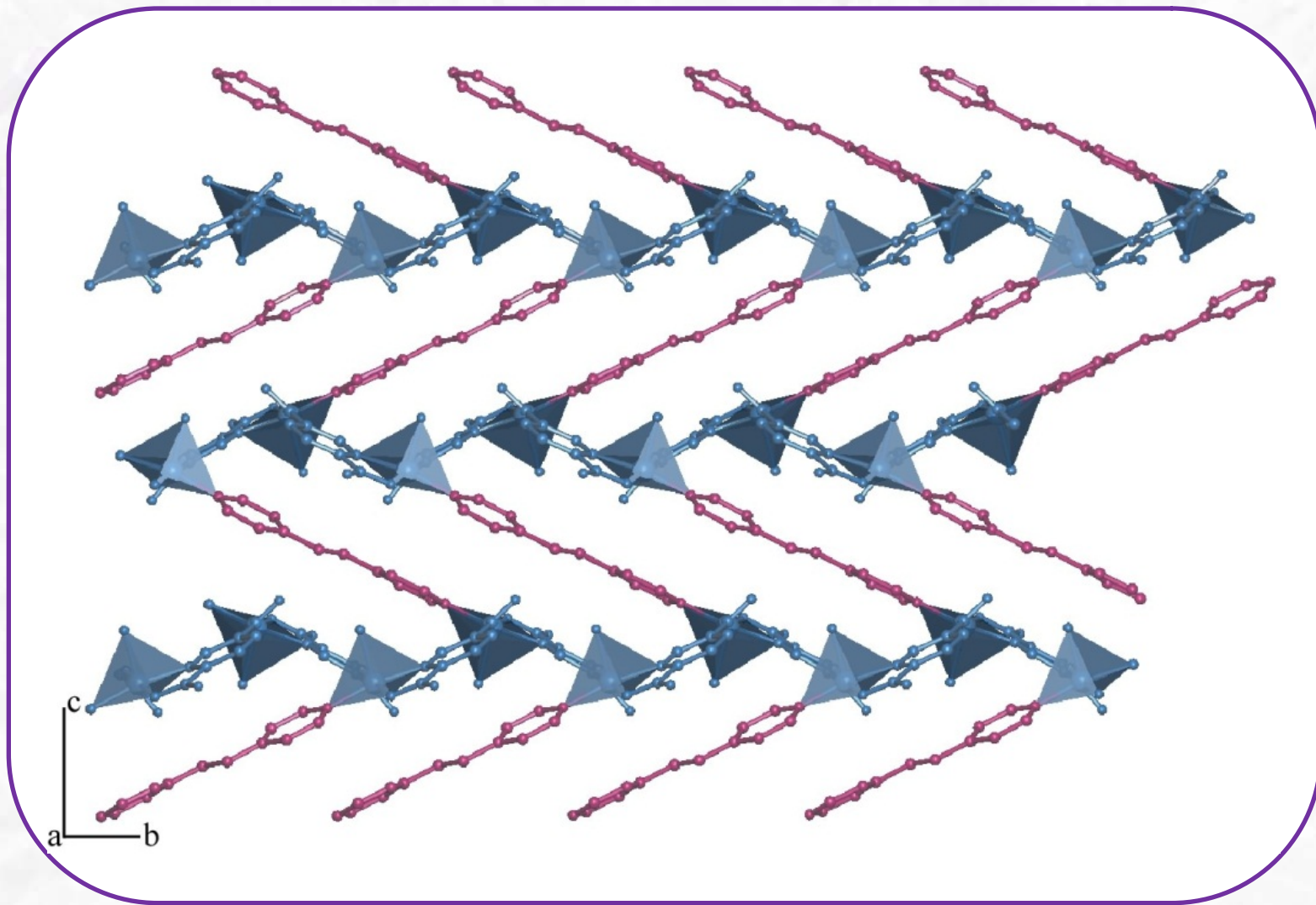
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Estructura Cristalina



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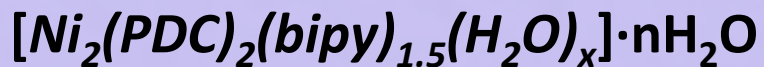


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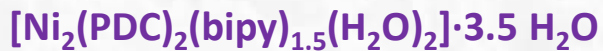
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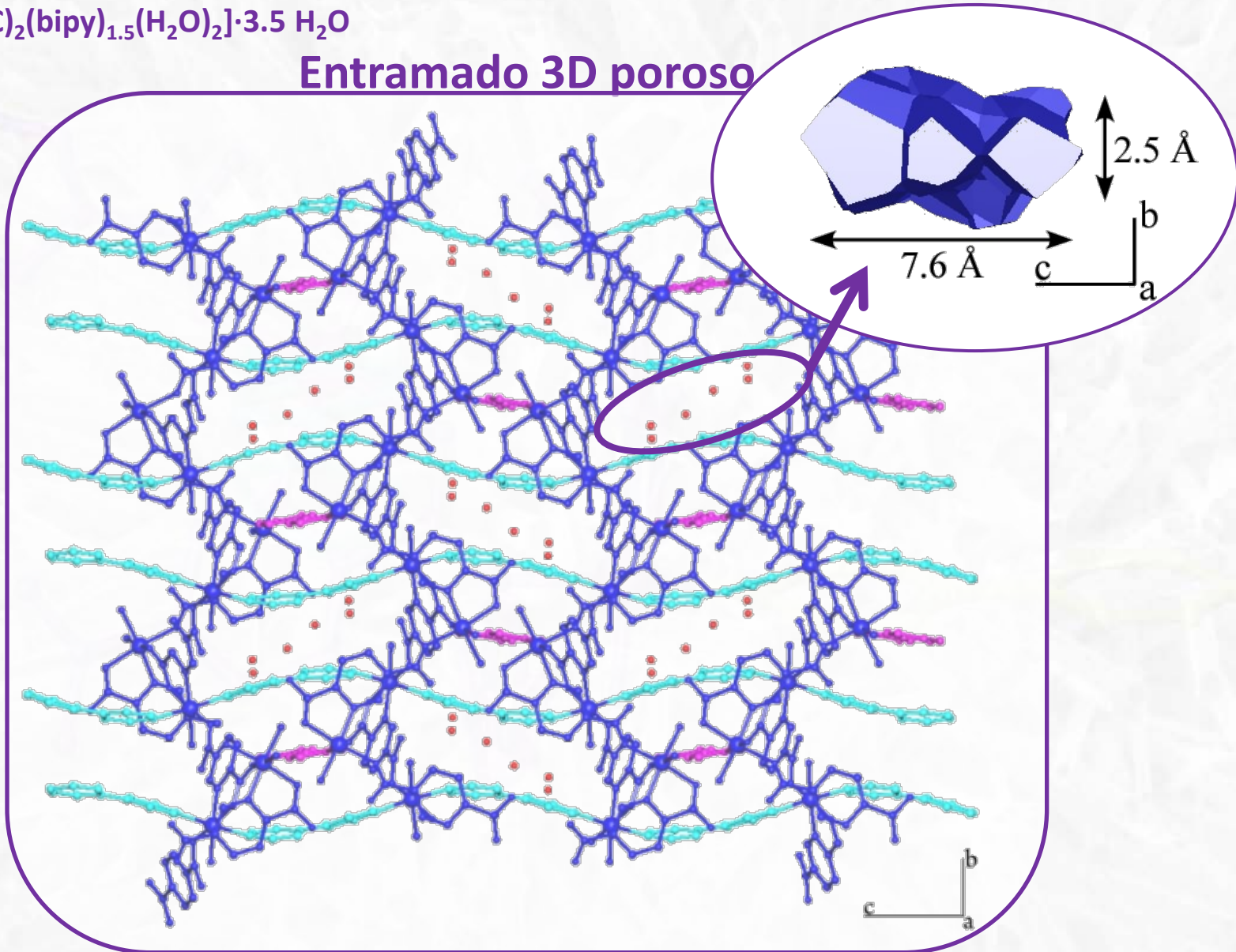
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Entramado 3D poroso



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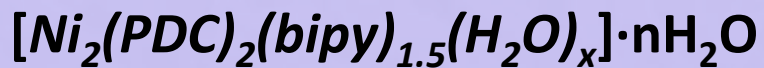


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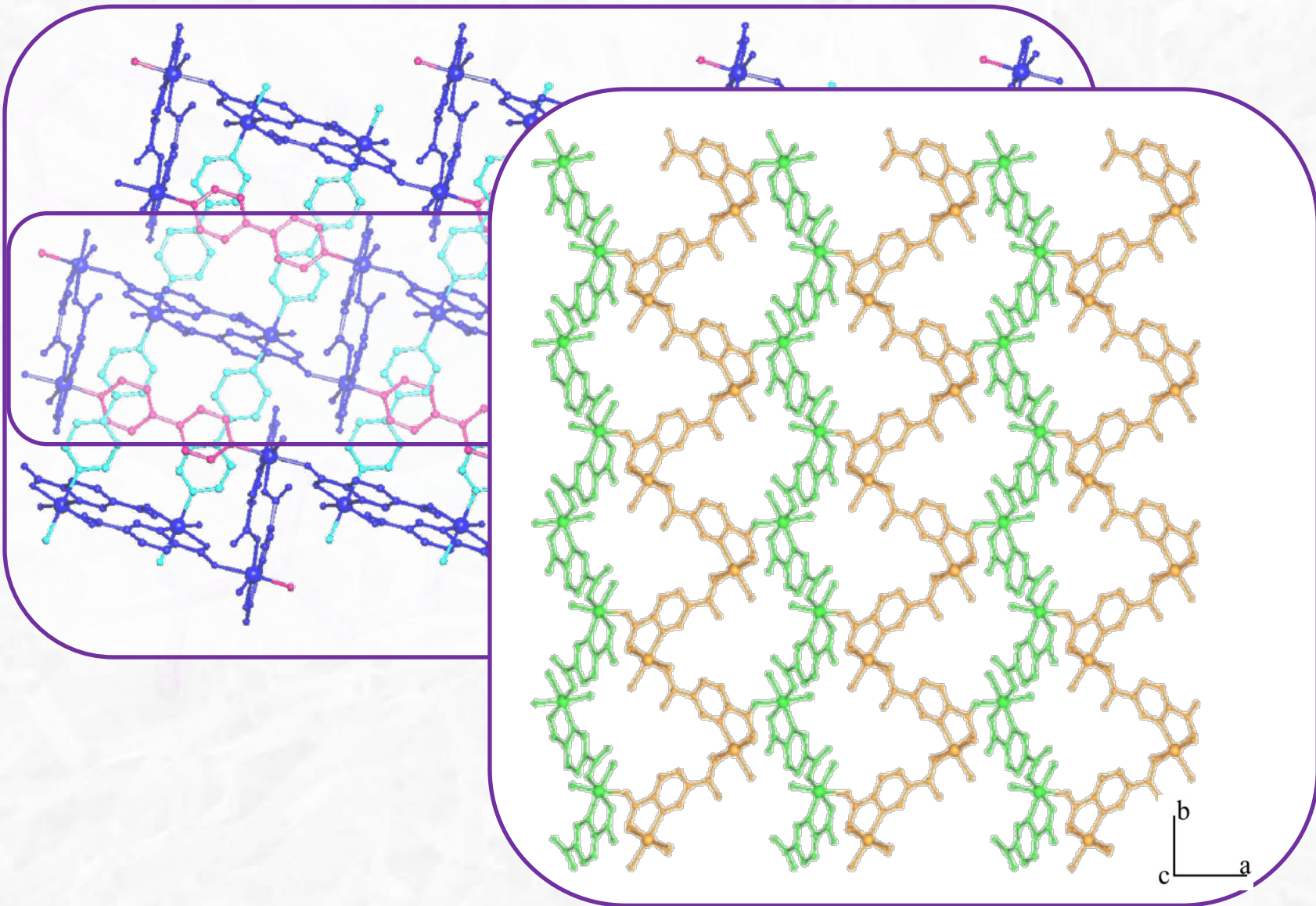
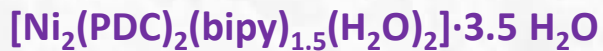
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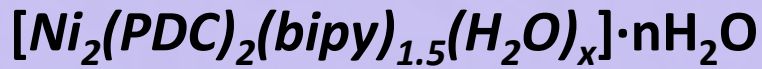


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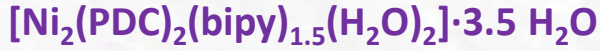
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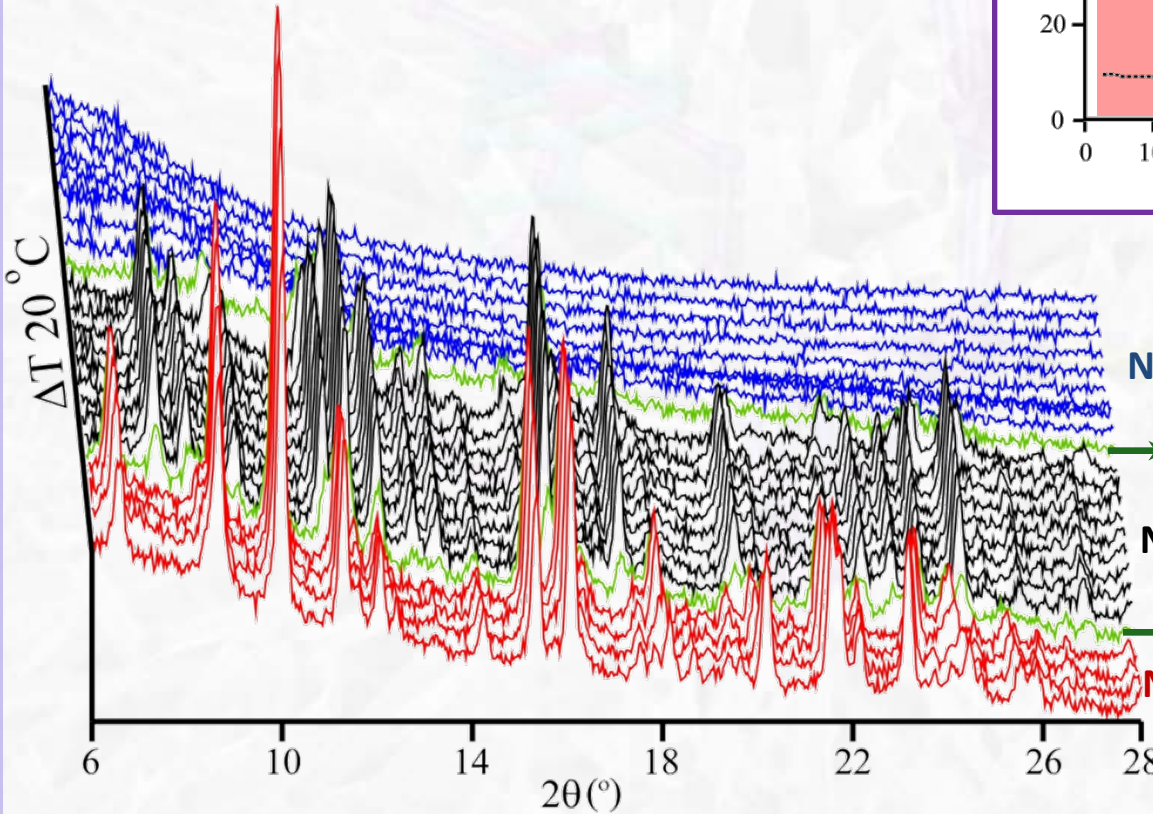
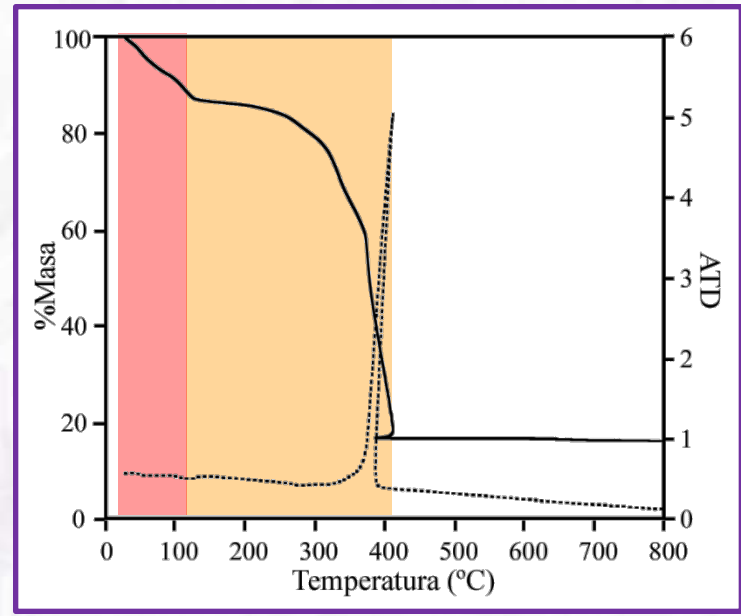
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Estudio Térmico



Transformación estructural
110°C



NiO

310 °C

NiPB1

110 °C

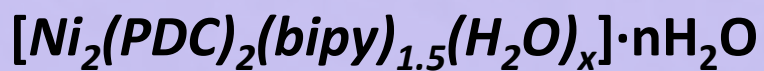
NiPB5.5

Transformación estructural

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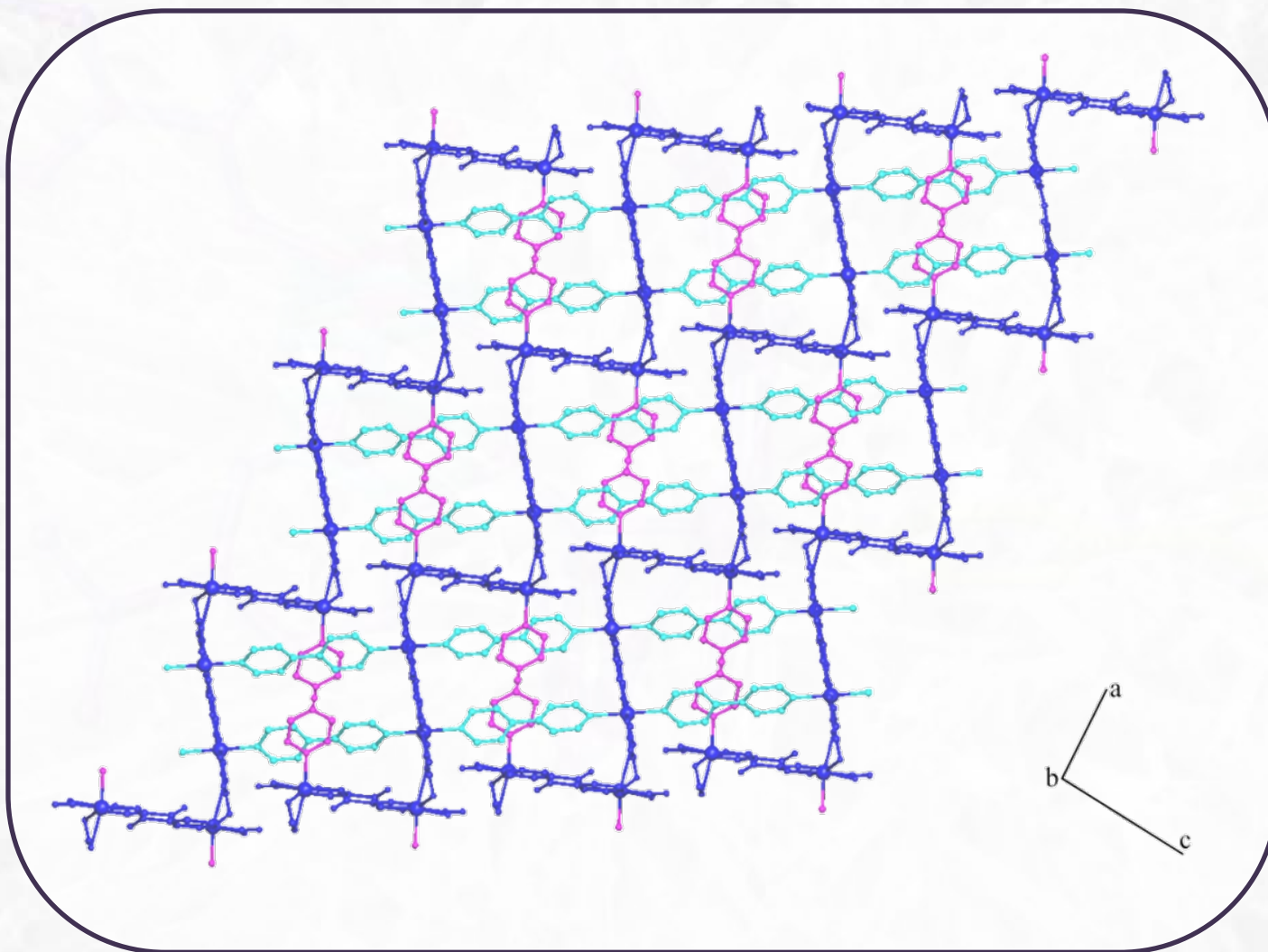
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Estructura Cristalina



Entramado 3D



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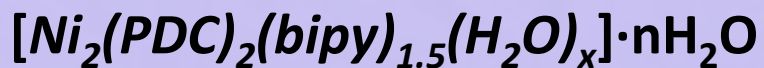


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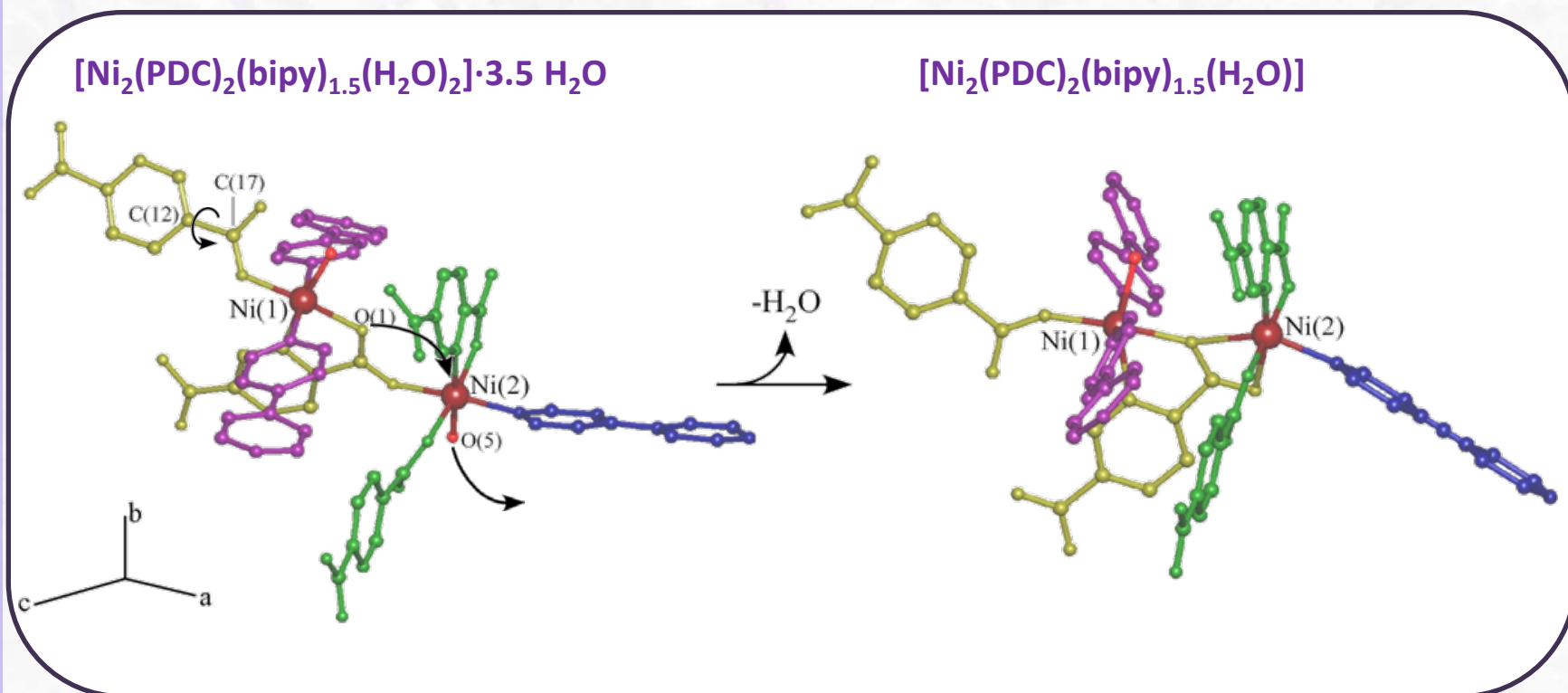
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Mecanismo de la transformación estructural



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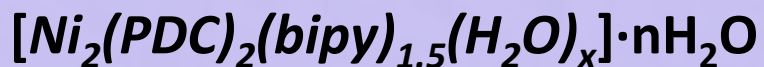


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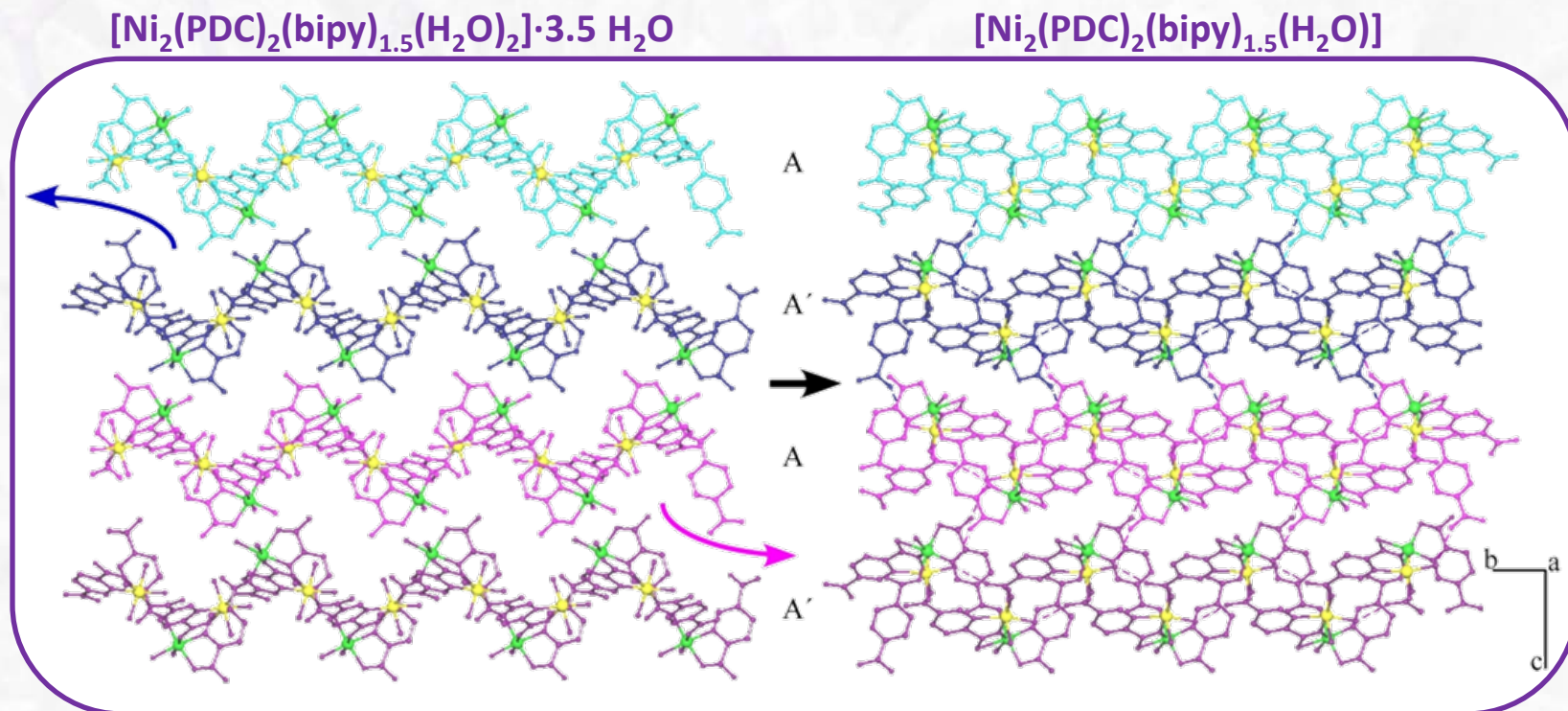


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Transformación Estructural

✓ Las características generales del apilamiento se conservan



Transformación estructural irreversible
Formación inusual de nuevos enlaces M-O

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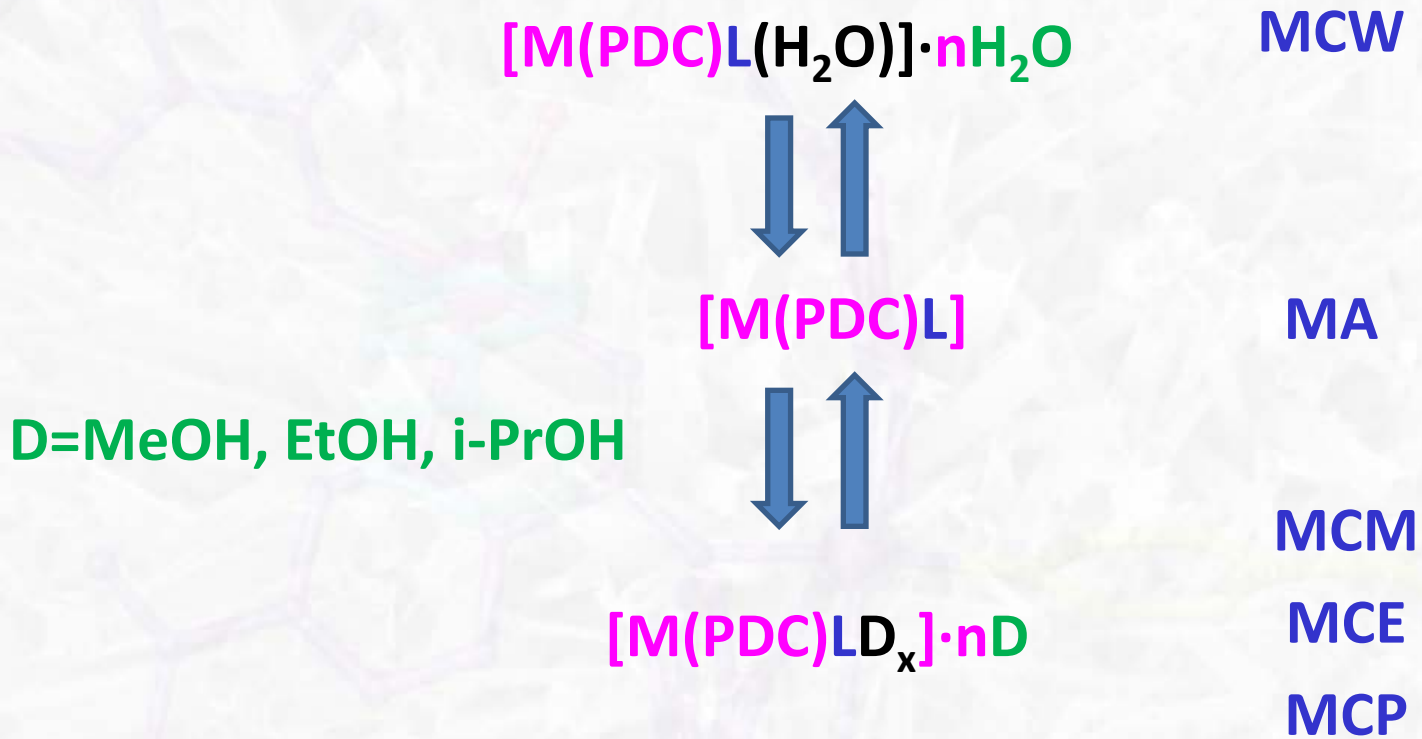


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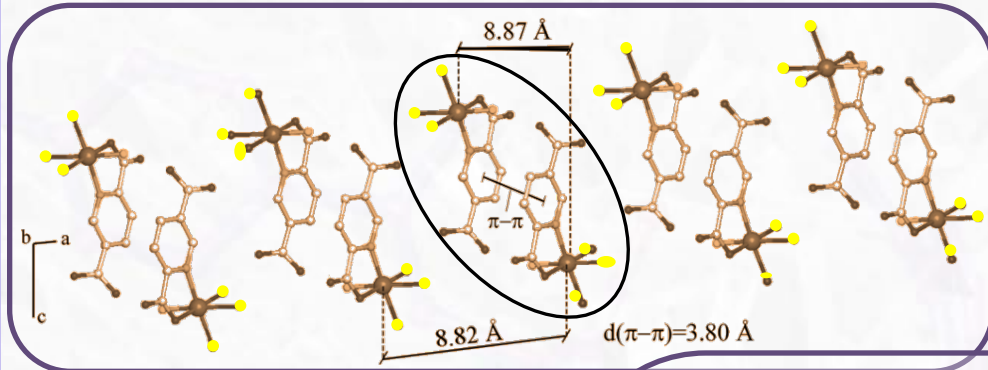


Solicitud de patente nº ID02335677.

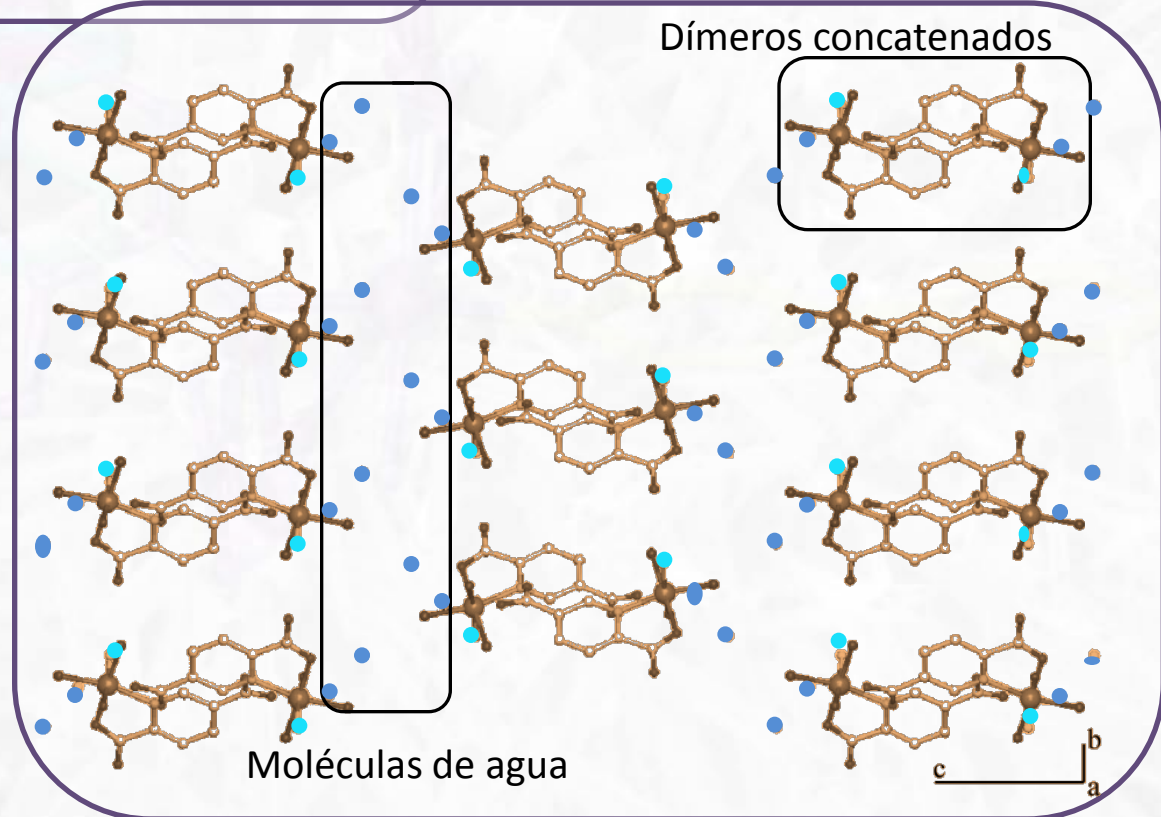
Arriortua M. I., Barandika M. G., Bazán B., Calderón-Casado A. y M. K. Urriaga (UPV/EHU), 2011.



Monómeros que se unen en asociaciones diméricas



MCW



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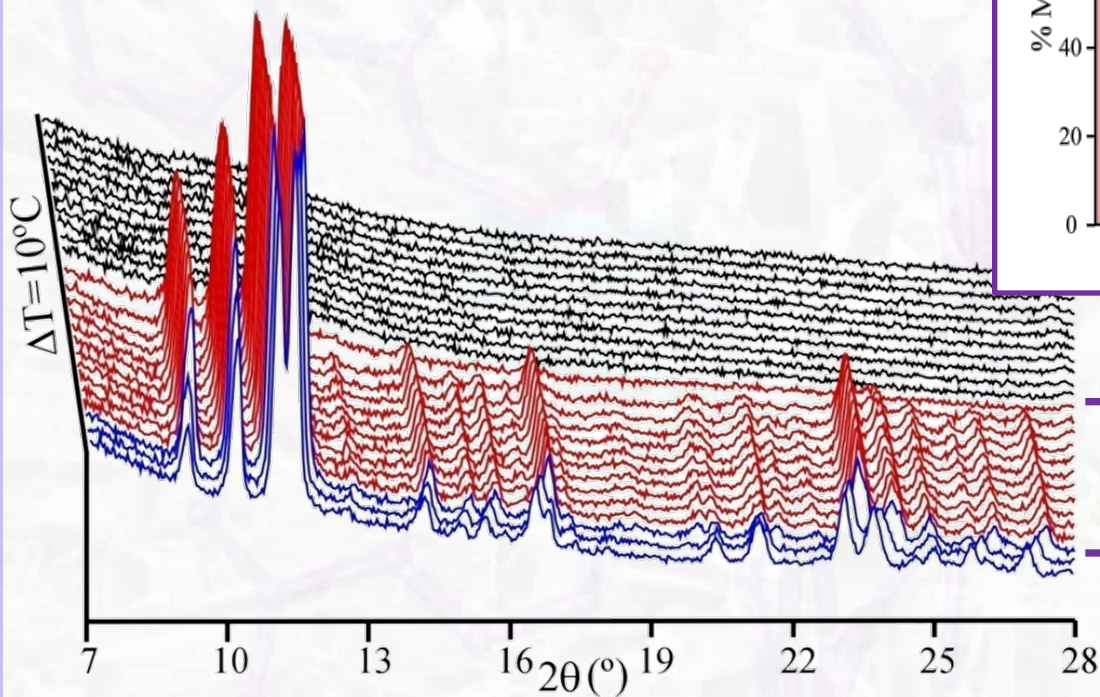


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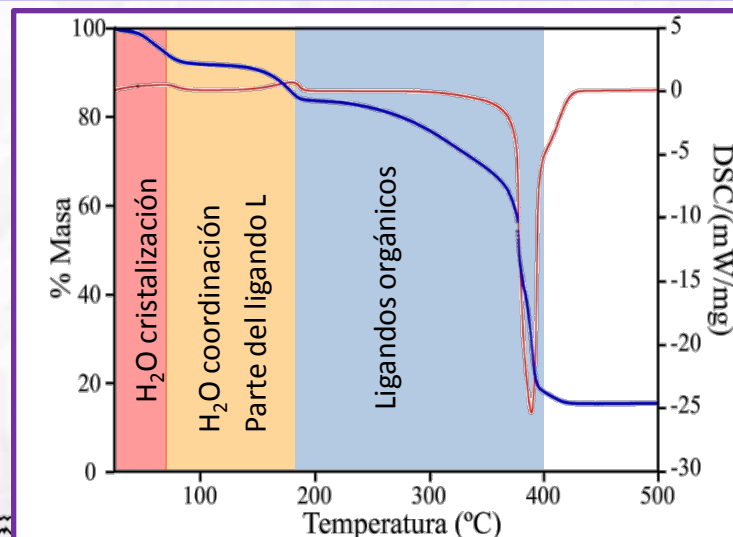
Estudio Térmico

MCW



→ 170 °C 2ª Transformación

→ 70 °C 1ª Transformación



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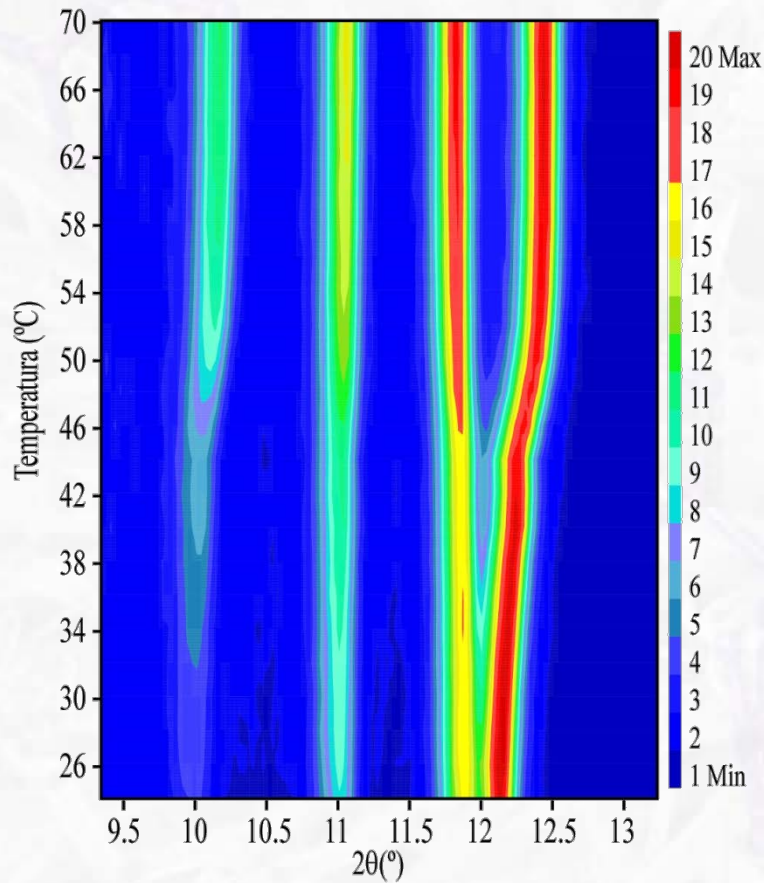
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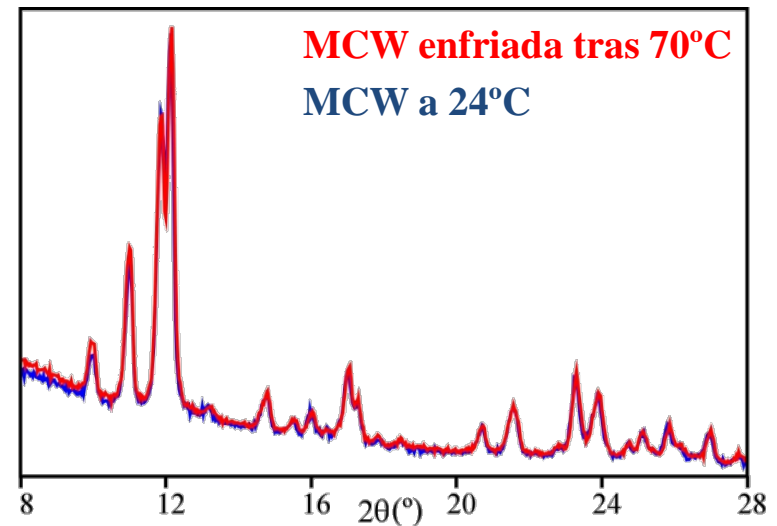
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Termodifractometría: 1ª transformación



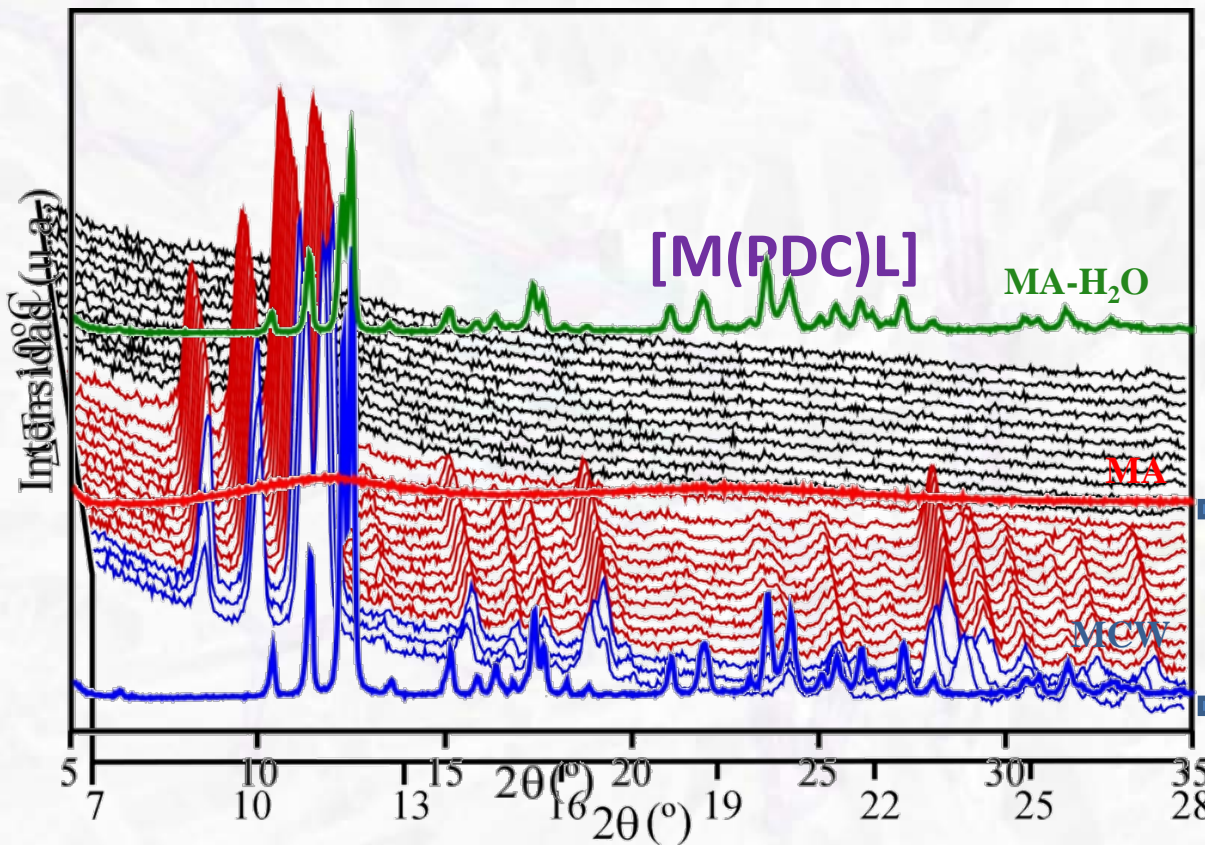
1ª Transformación: deshidratación

Reversible al contacto con la atmósfera



deshidratación reversible

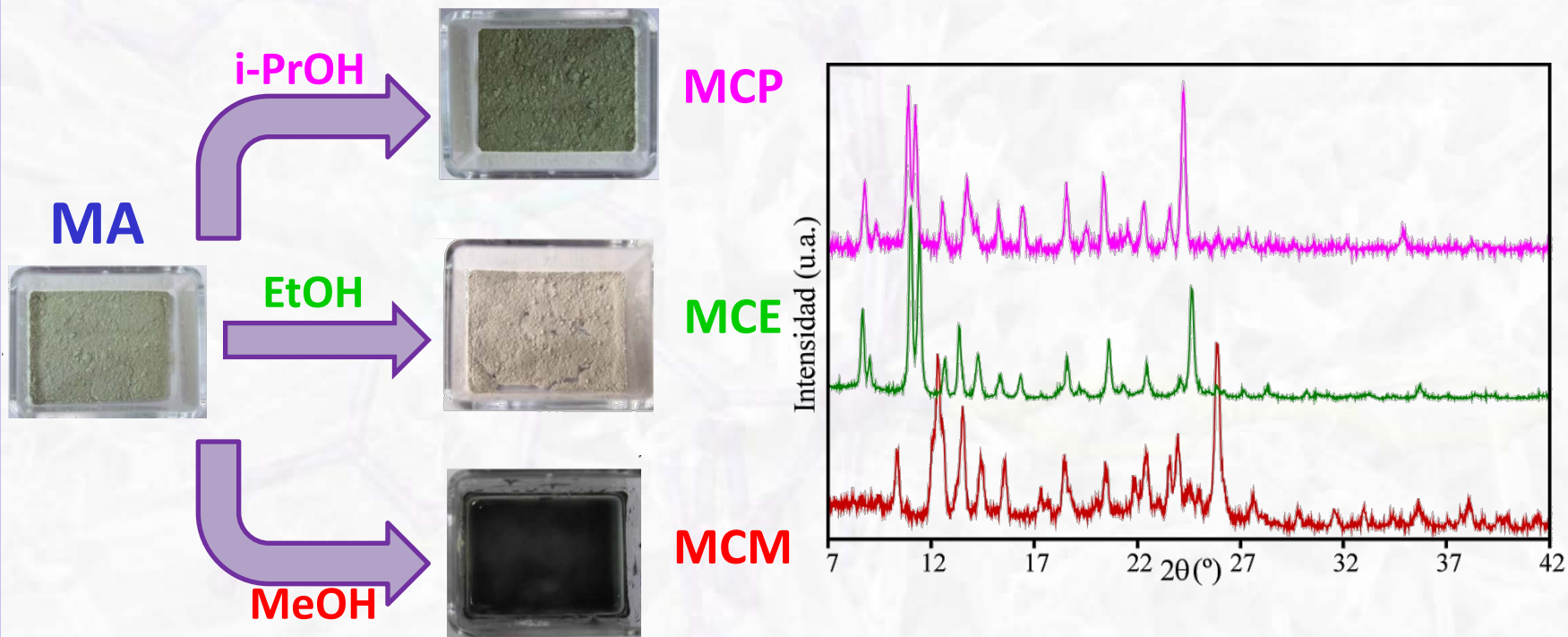
Termodifractometría: 2ª transformación



MCW

amorfización reversible

- Estudio de la absorción de tres alcoholes sobre la fase MA



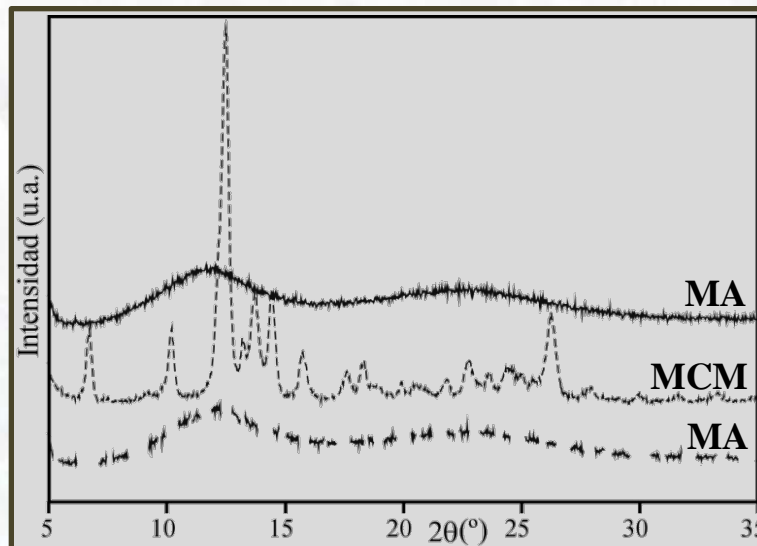
- Difracción de rayos X en muestra policristalina

→ Todas las fases son cristalinas y diferentes

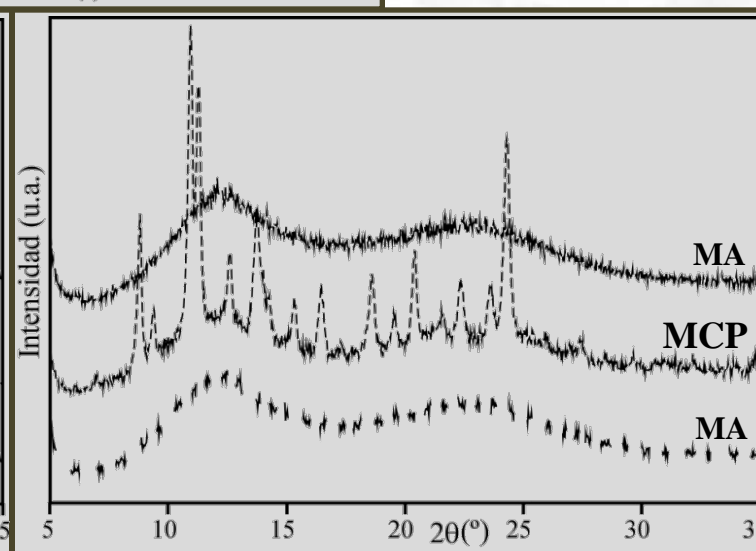
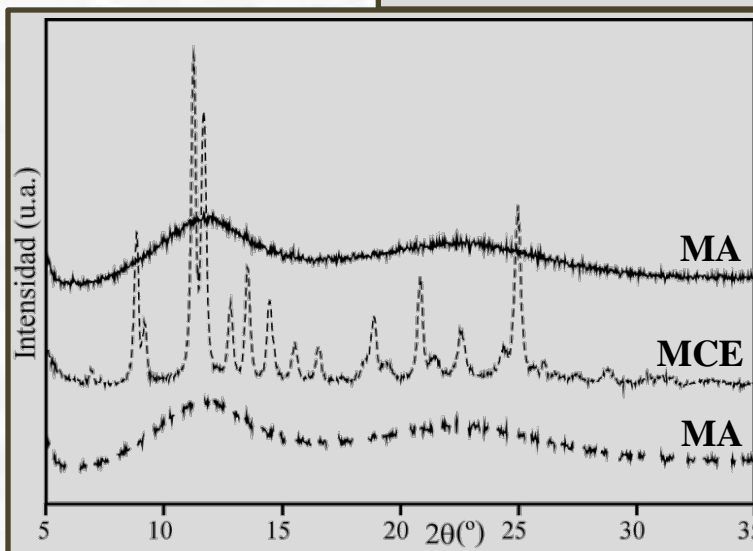
→ Fases MCE y MCP muy similares

• Reversibilidad del proceso (difracción de rayos X)

180°C



- Reiterada
- Reutilizable

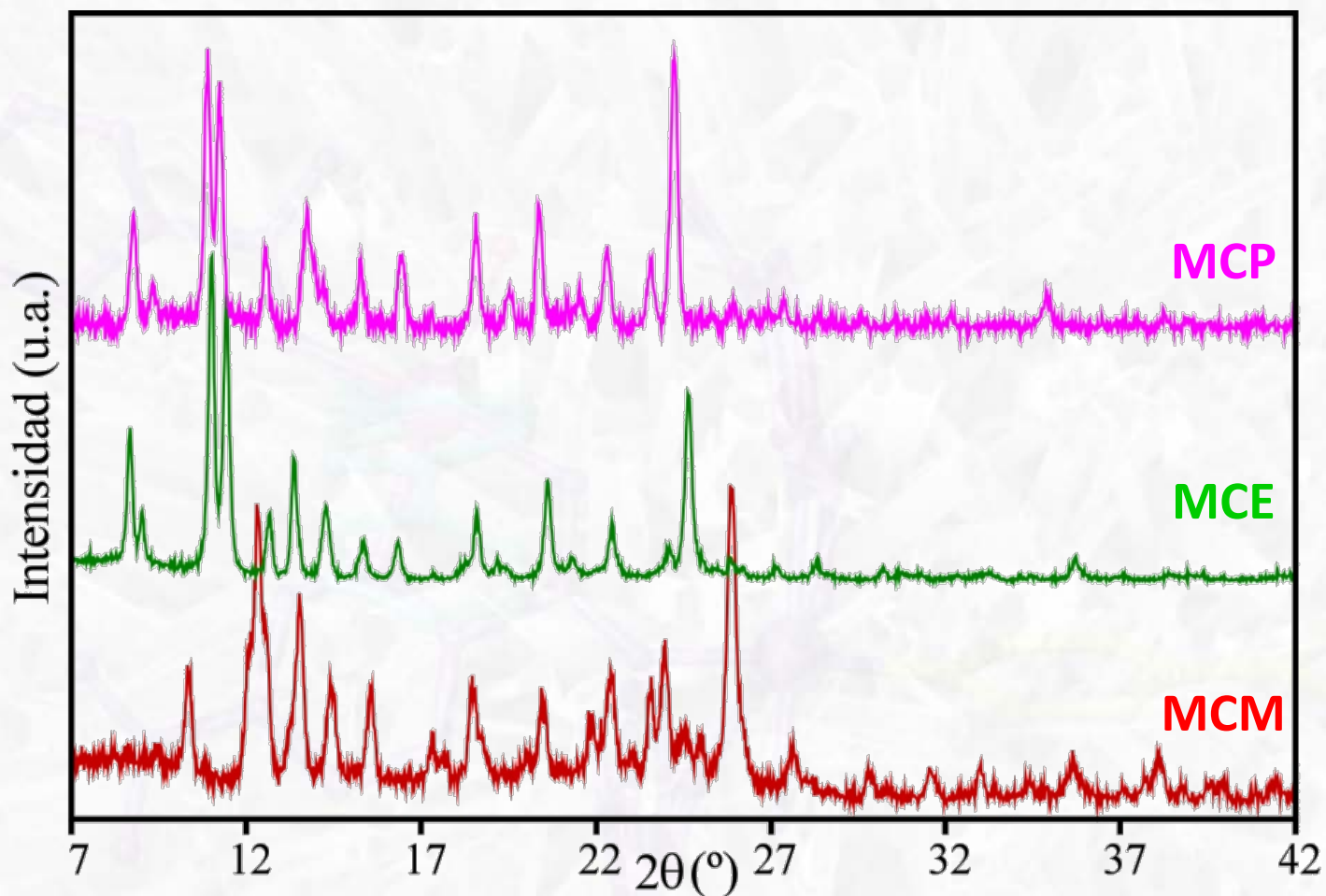


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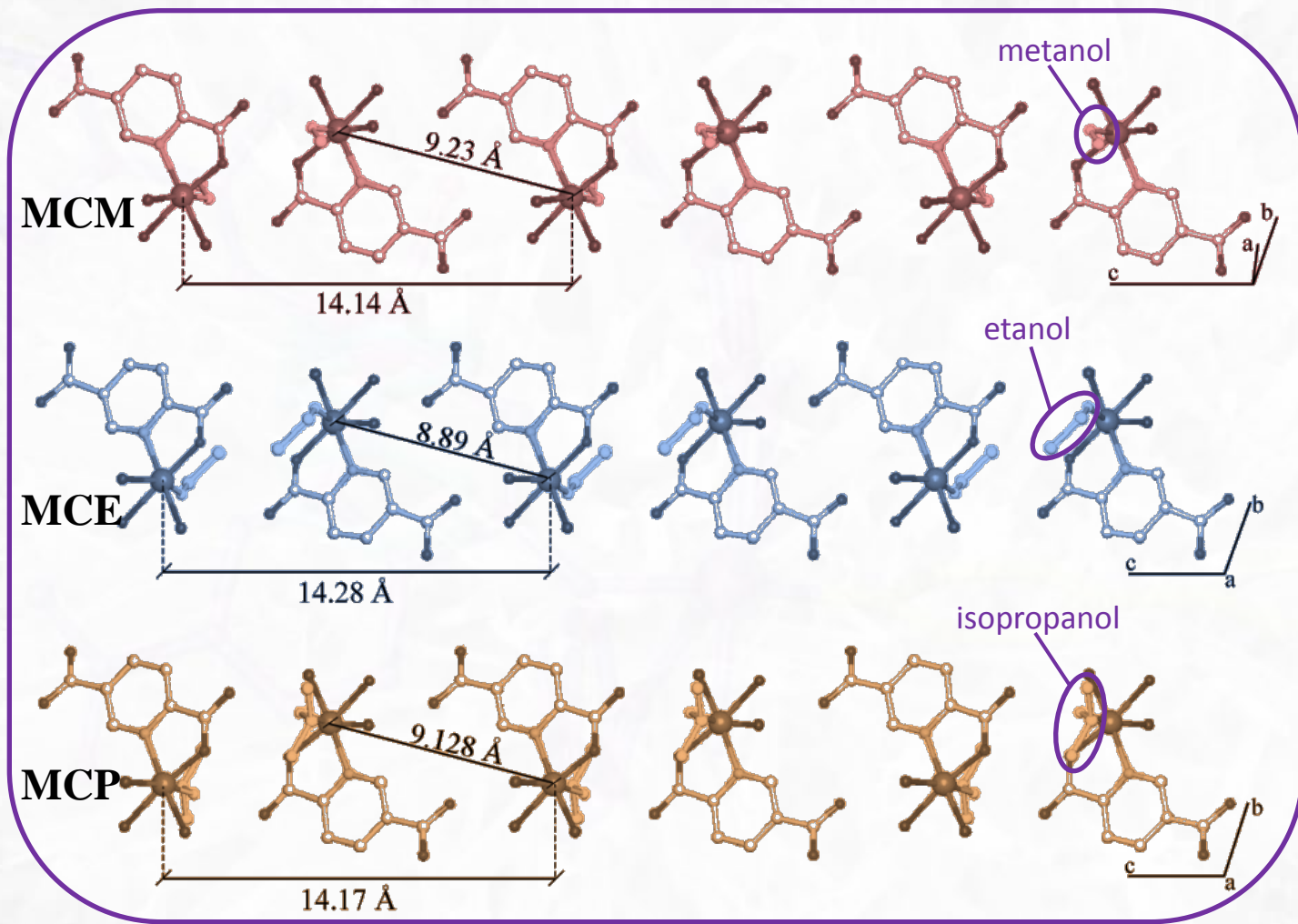
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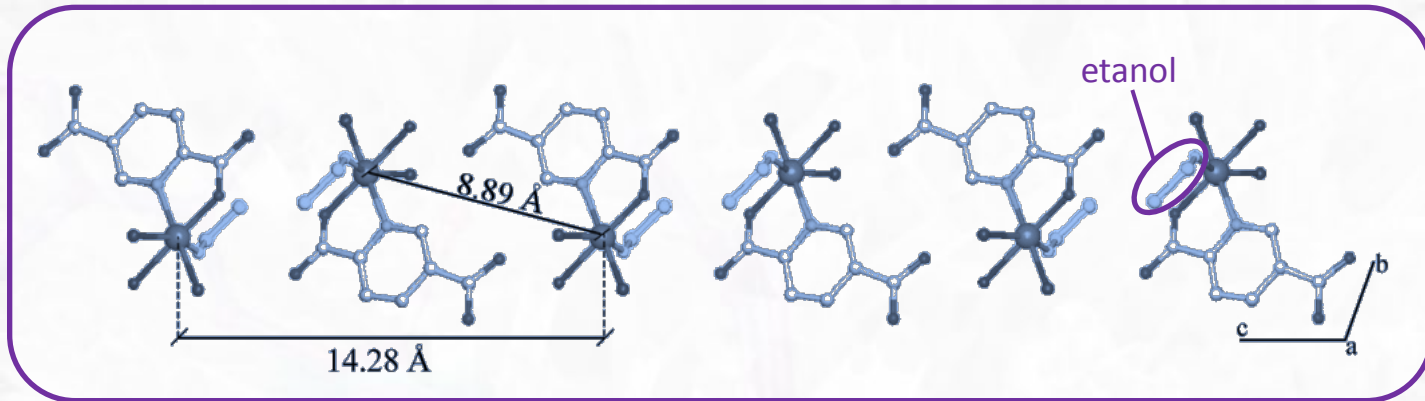
- Recristalización de las fases

Monómeros concatenados

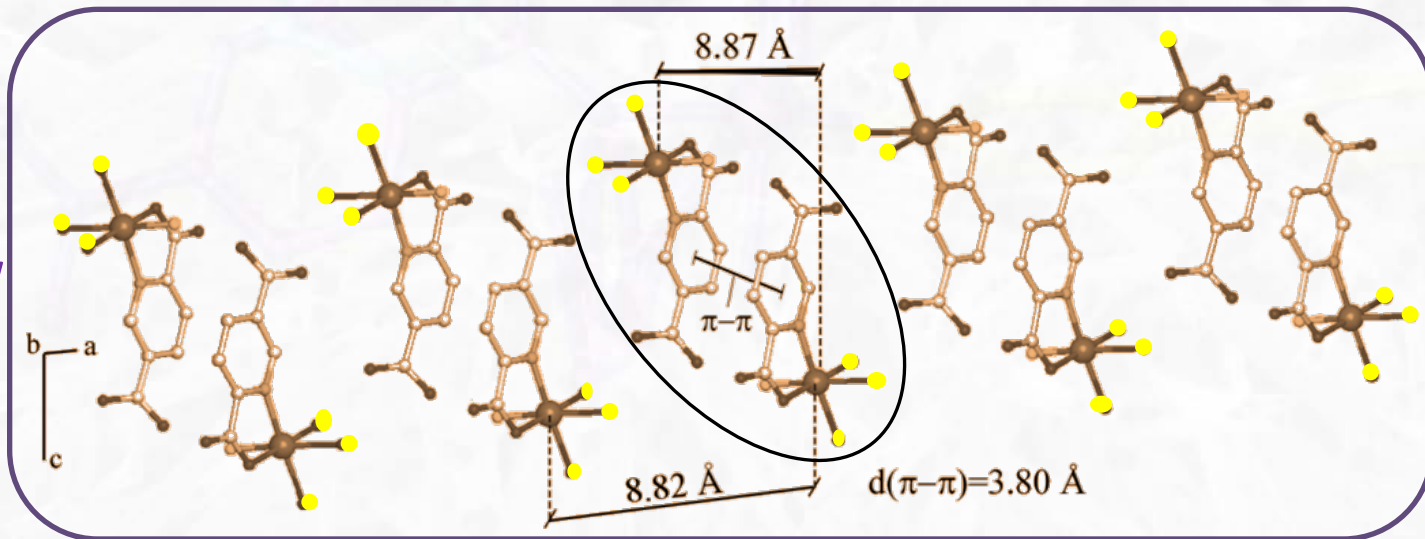


Cambios de color (UV-Vis)

MCE



MCW



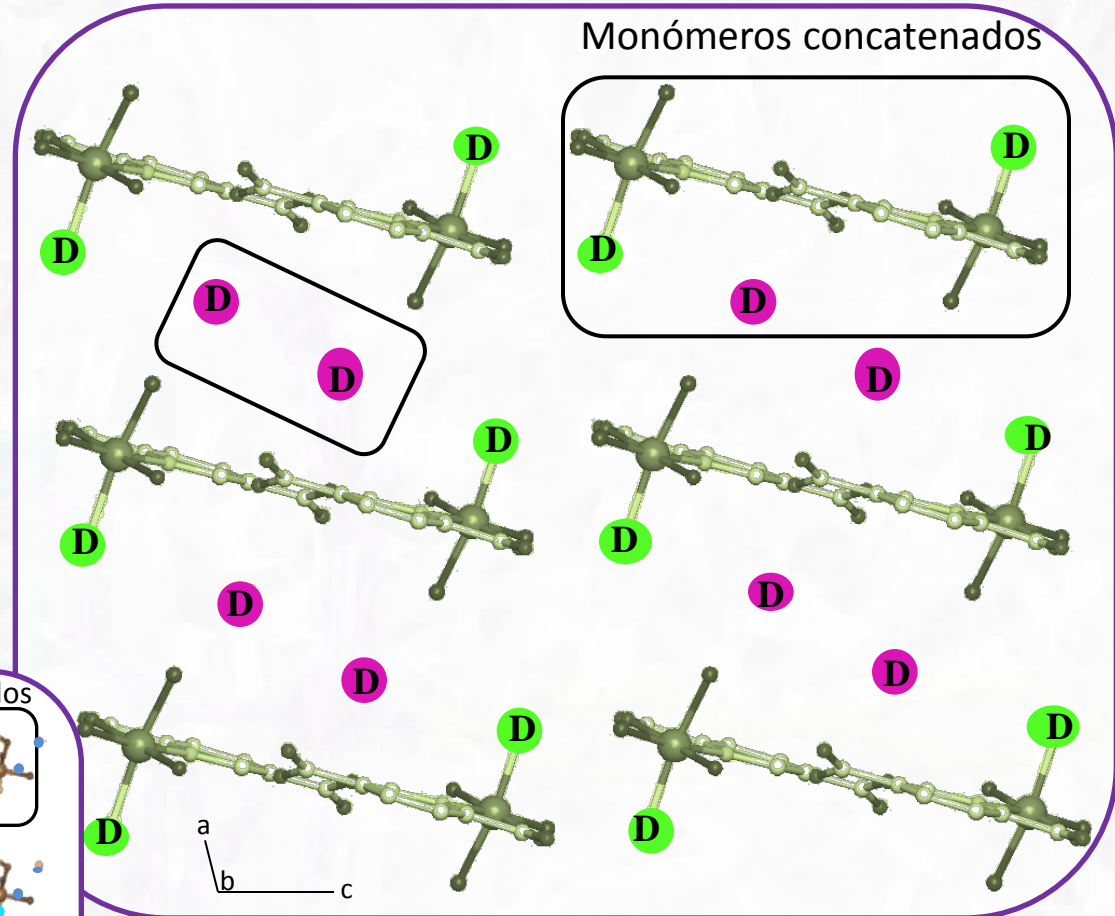
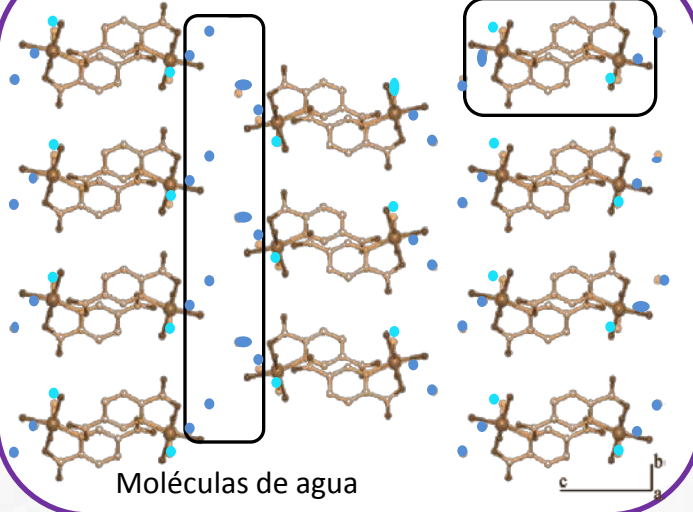


Estructura Cristalina

D
MeOH \rightarrow MCM
EtOH \rightarrow MCE
iPrOH \rightarrow MCP

MCW

Dímeros concatenados

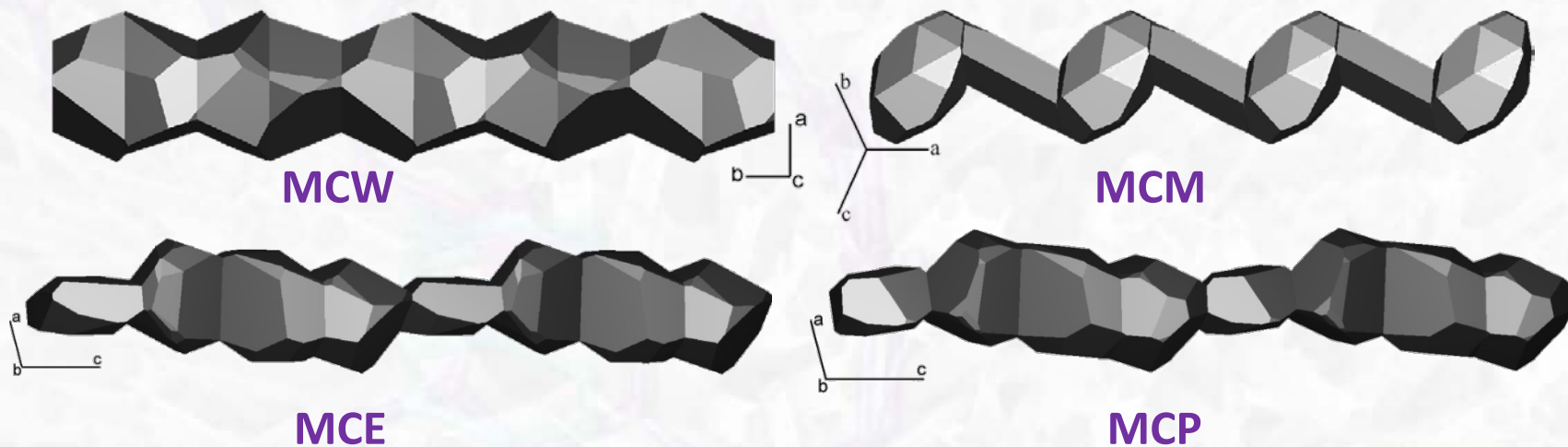


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Estudio de los canales \rightarrow poliedros de Voronoi-Dirichlet



Compuesto	MCW	MCM	MCE	MCP
$D_{\text{máx}}$ (Å)	3.1	4.3	4.3	4.2
$D_{\text{mín}}$ (Å)	3.1	3.0	3.4	3.1



Efecto sinérgico de 3 procesos:

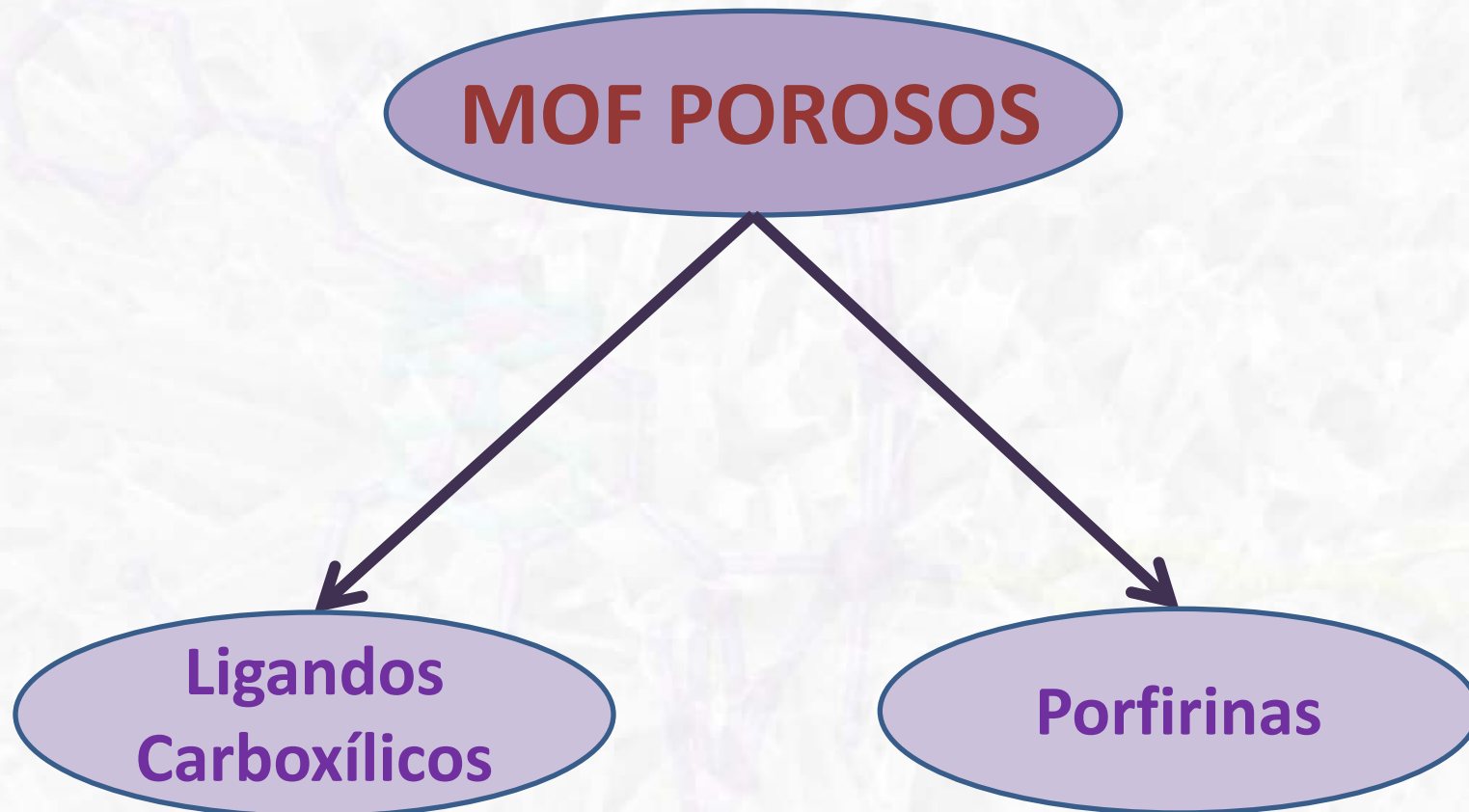
- Cambio en la coordinación de L
- Absorción-desorción de D en esfera de coordinación
- Absorción-desorción de D en cavidades MOF poroso



Cambios de color

Sensor de agua y tres alcoholes





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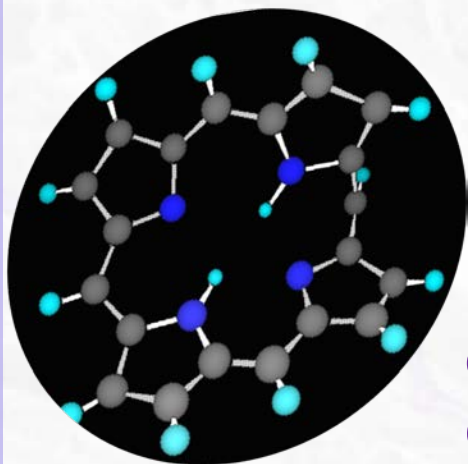


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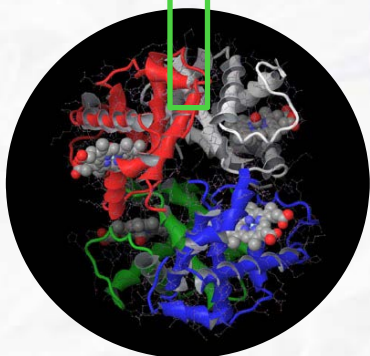
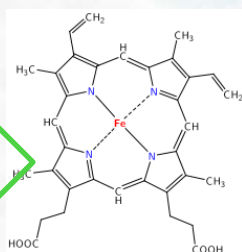
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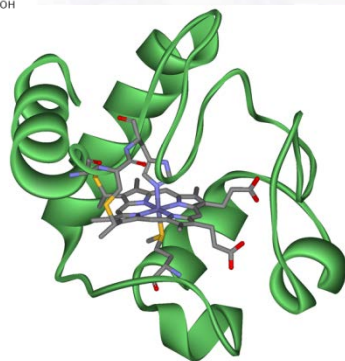
Las porfirinas son macrociclos tetrapirrólicos



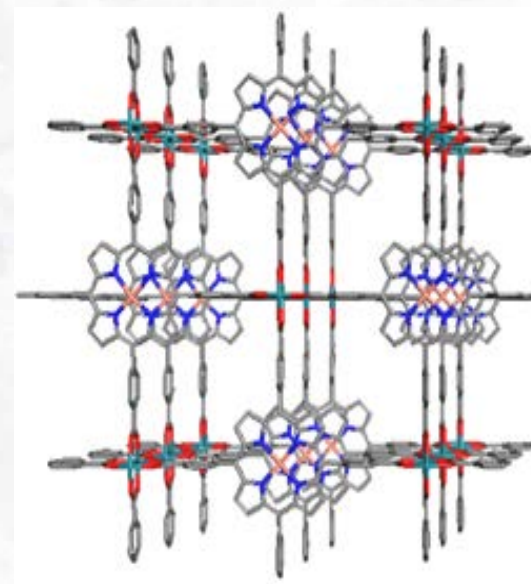
Forman entidades supramoleculares que se coordinan a ligandos axiales o a ligandos externos de los macrociclos



HEMOGLOBINA



CITOCROMO



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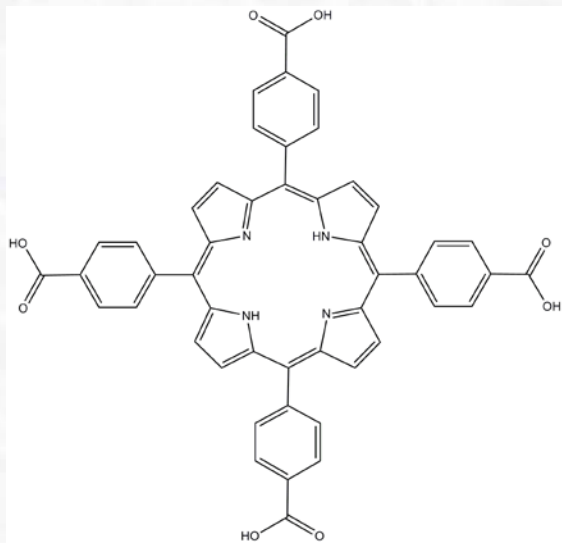


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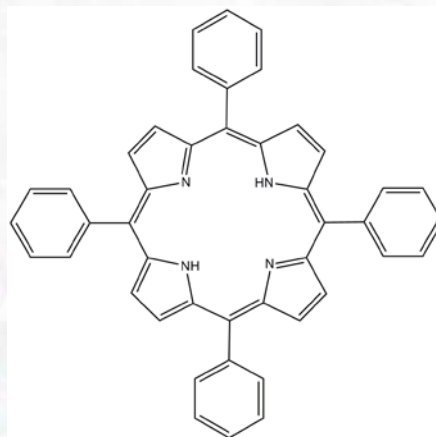
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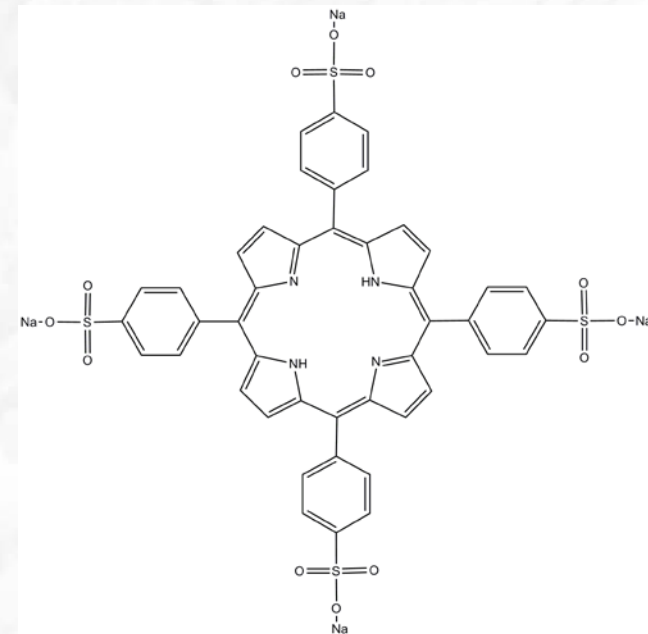
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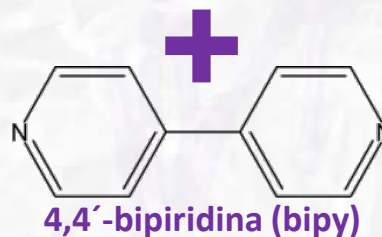
meso-tetra-4-carboxifenilporfirina
(TCPP)



meso-tetra-4-fenilporfirina
(TPP)



Sal tetrasódica de la *meso*-
tetrafenilporfirina ácido tetrasulfónico
(TPPS)



4,4'-bipiridina (bipy)



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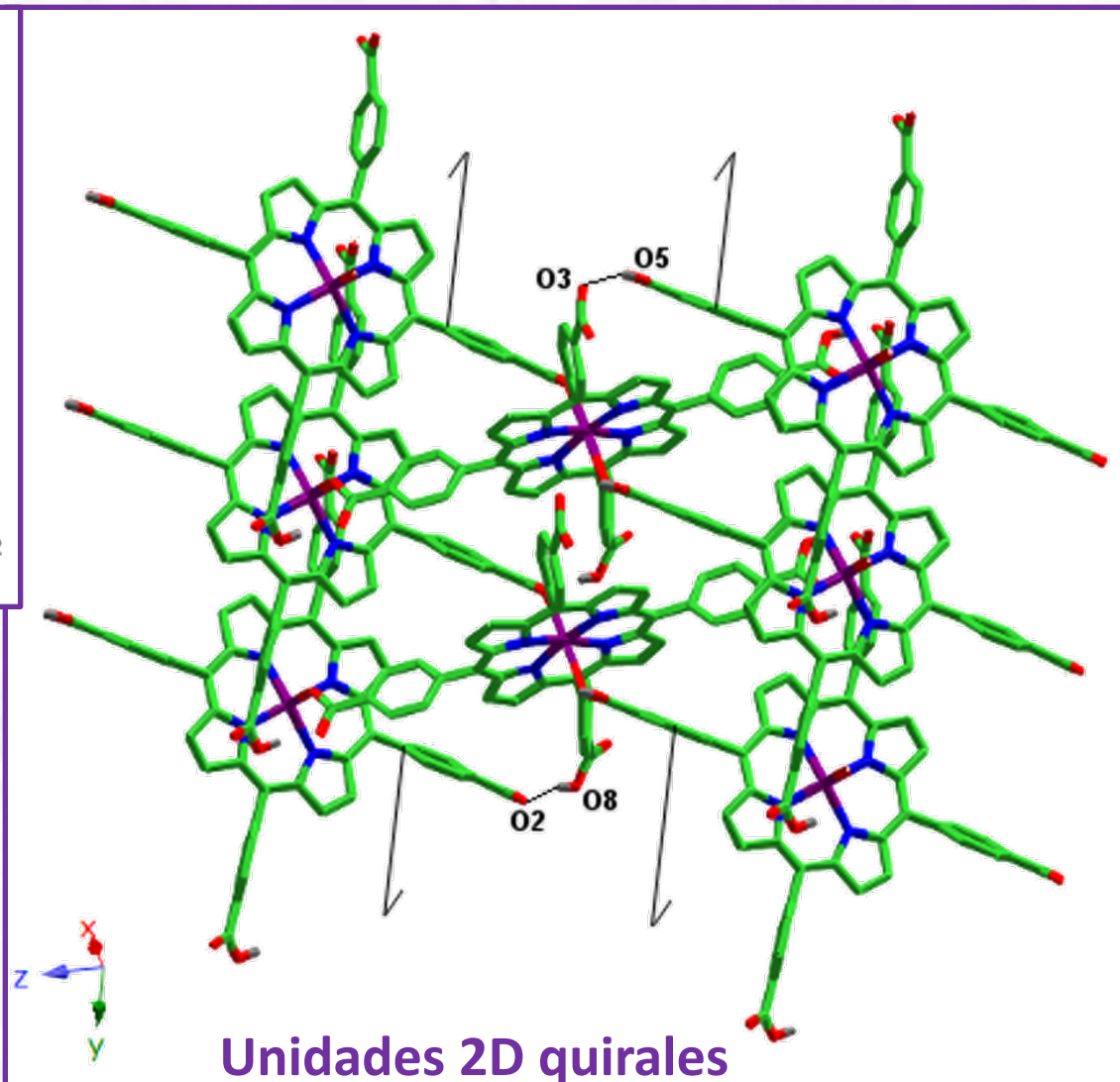
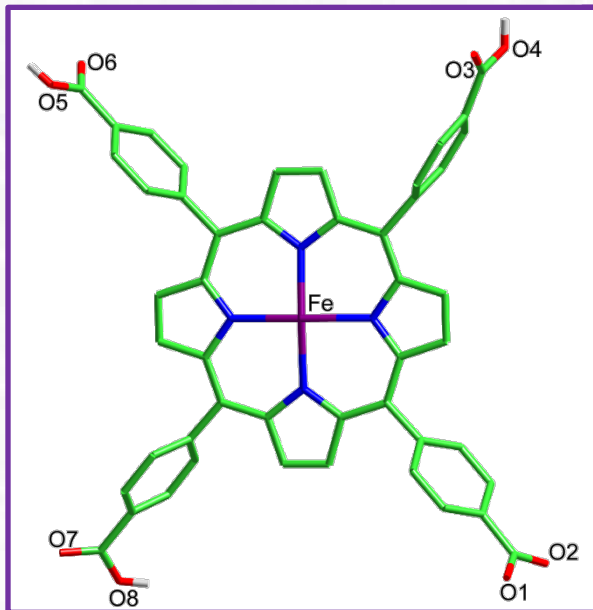
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- *meso*-tetra-4-carboxifenilporfirina (TCPP)



Unidades 2D quirales

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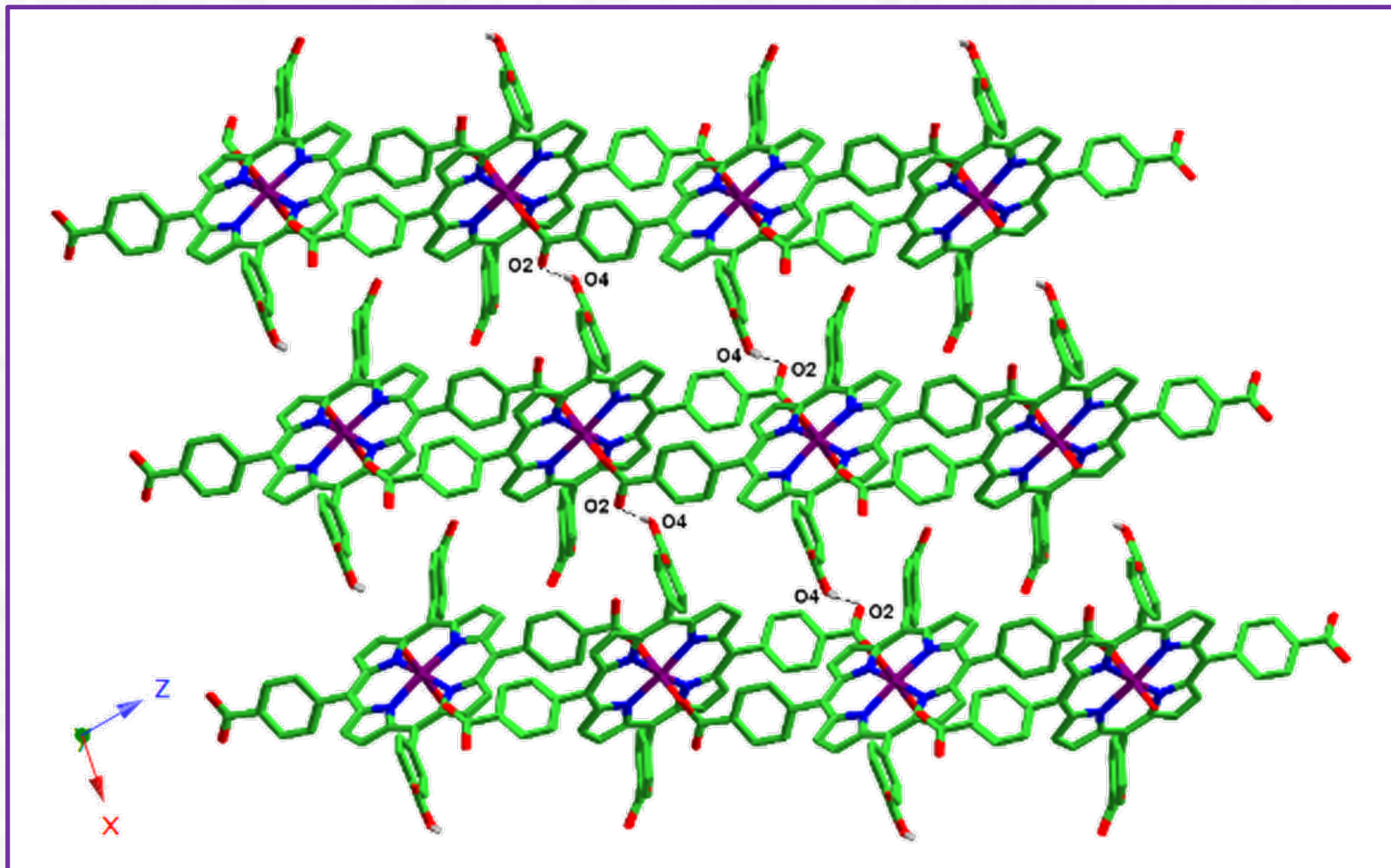


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La estructura 3D
preserva la quiralidad

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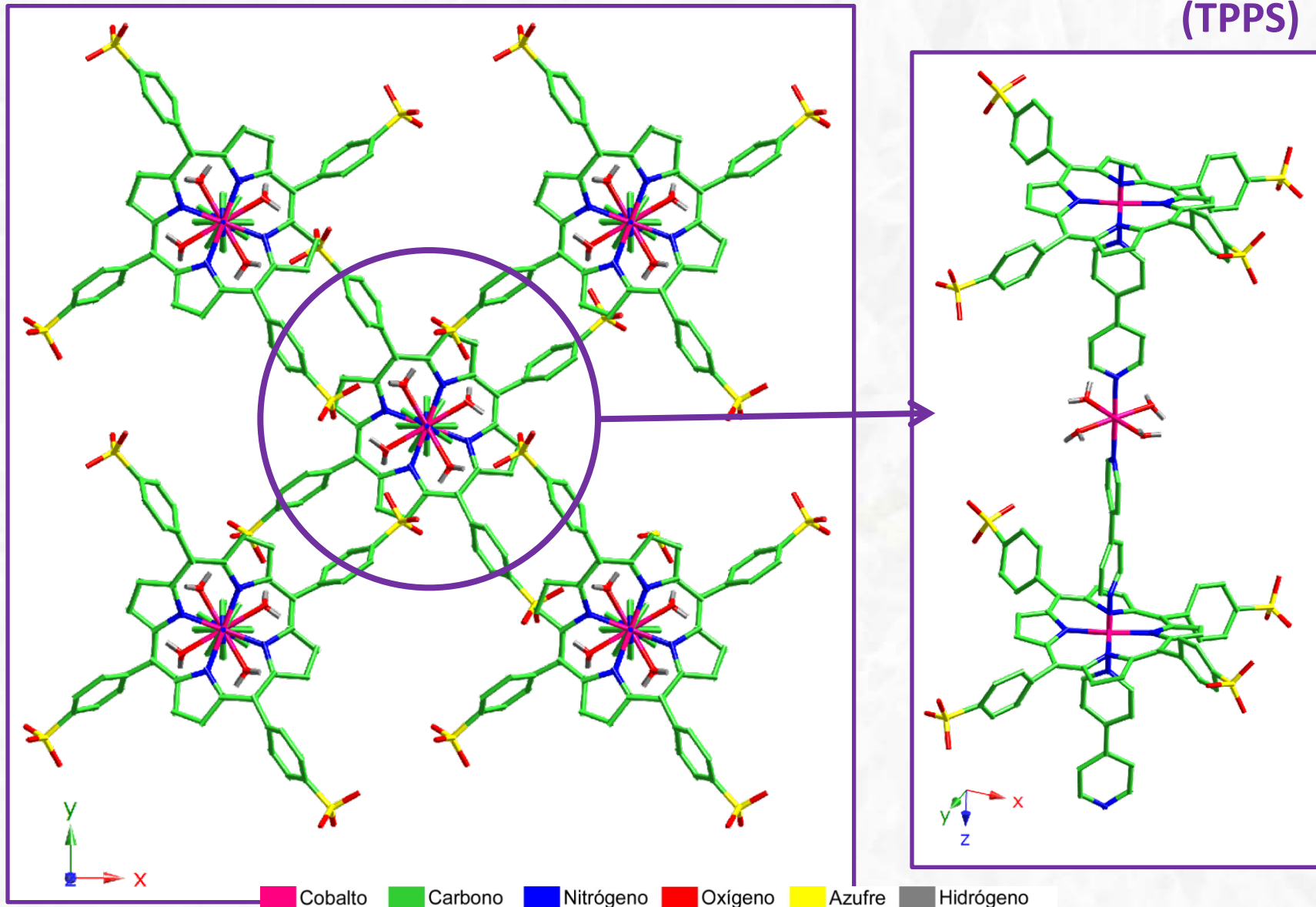


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- Sal tetrasódica de la *meso*-tetrafenilporfirina ácido tetrasulfónico (TPPS)



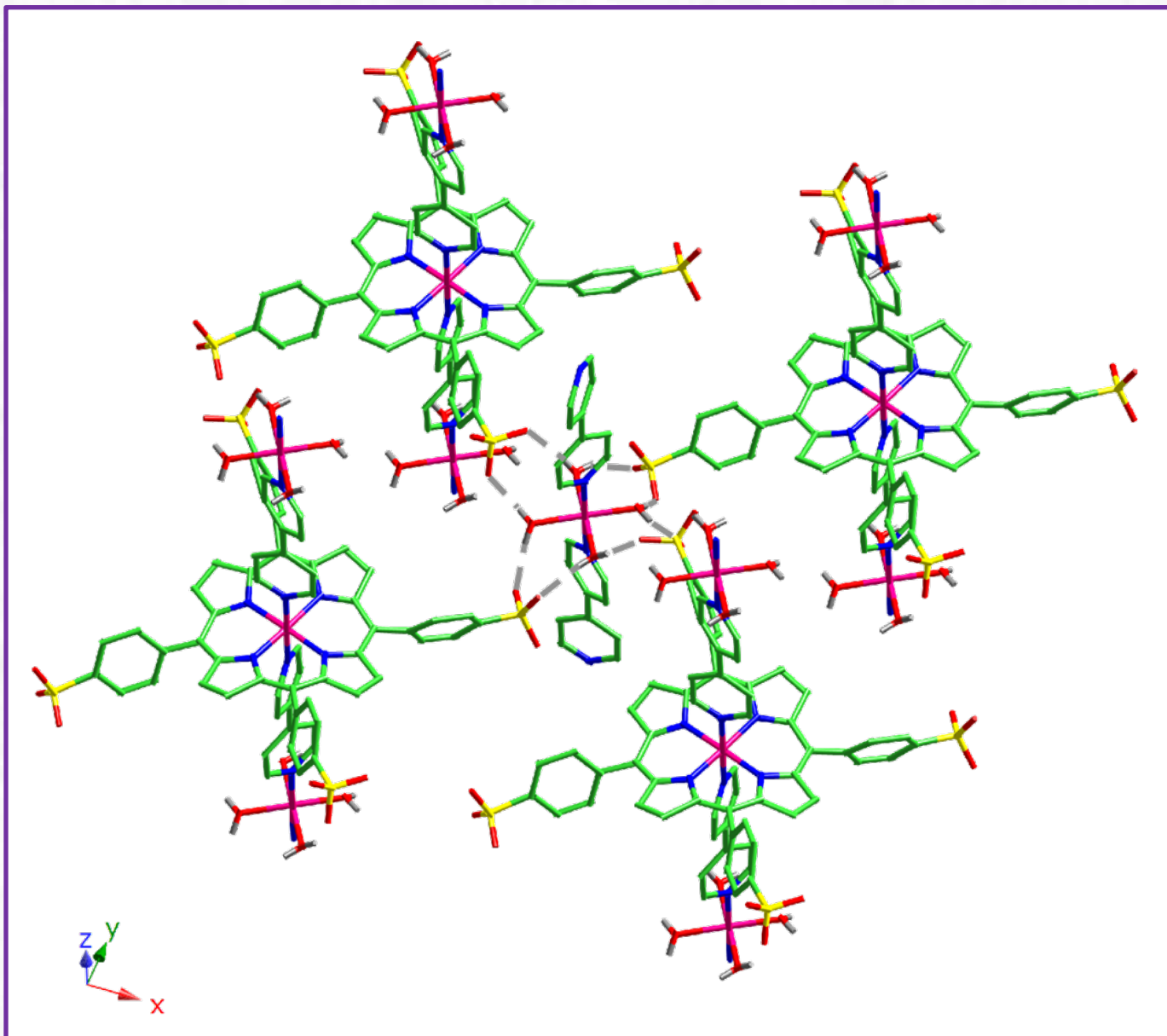
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Estructura Cristalina



- Cobalto
- Carbono
- Nitrógeno
- Oxígeno
- Azufre
- Hidrógeno

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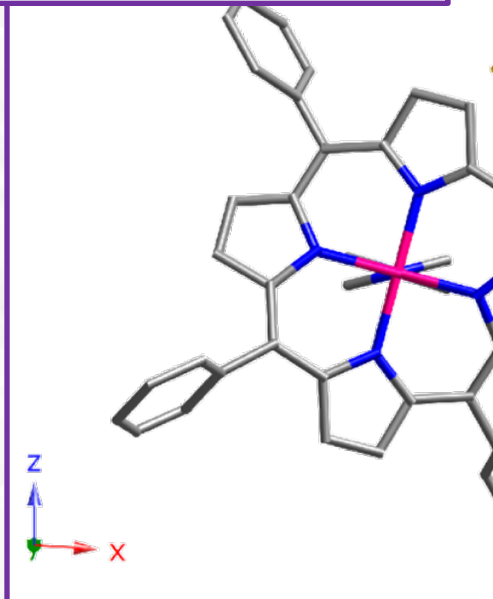
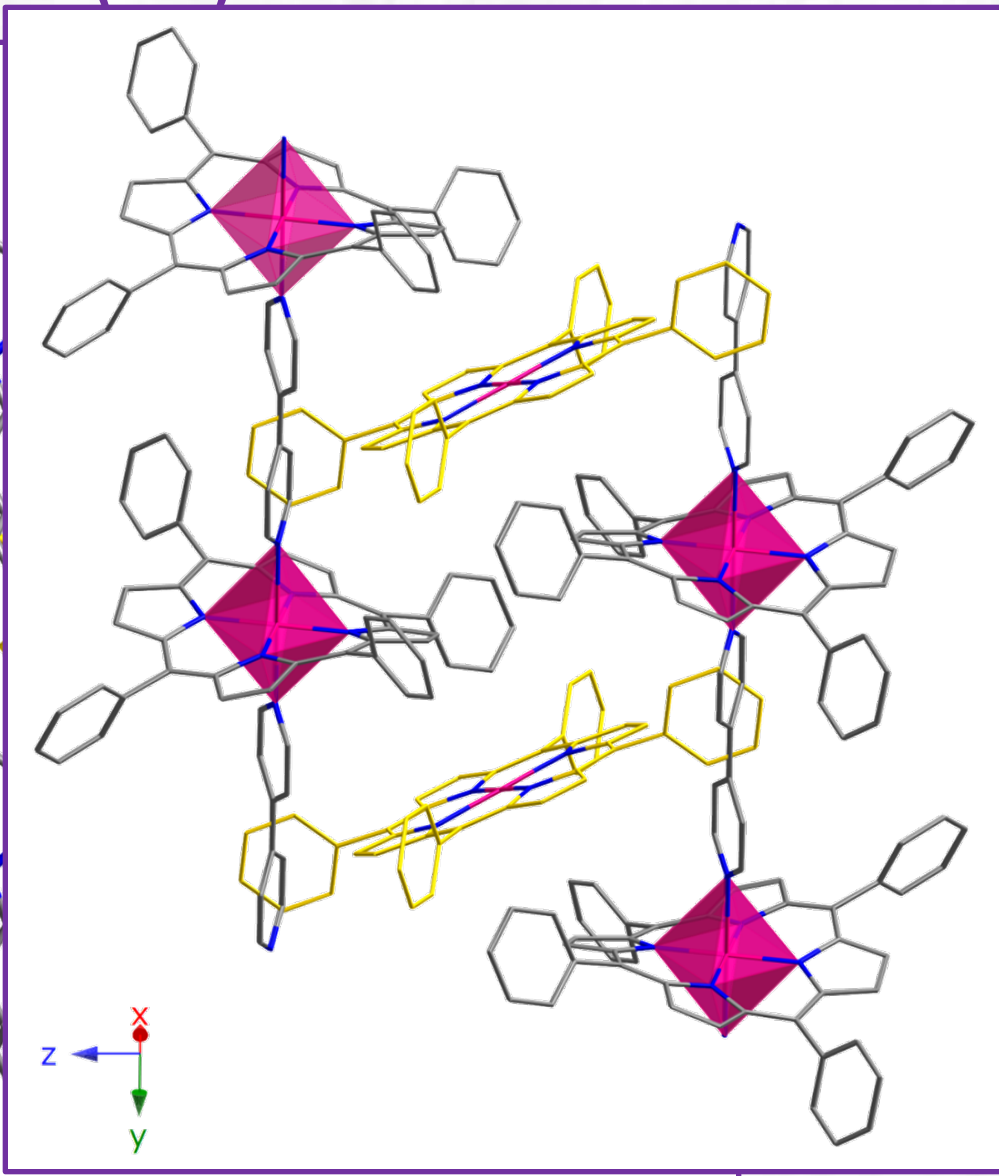
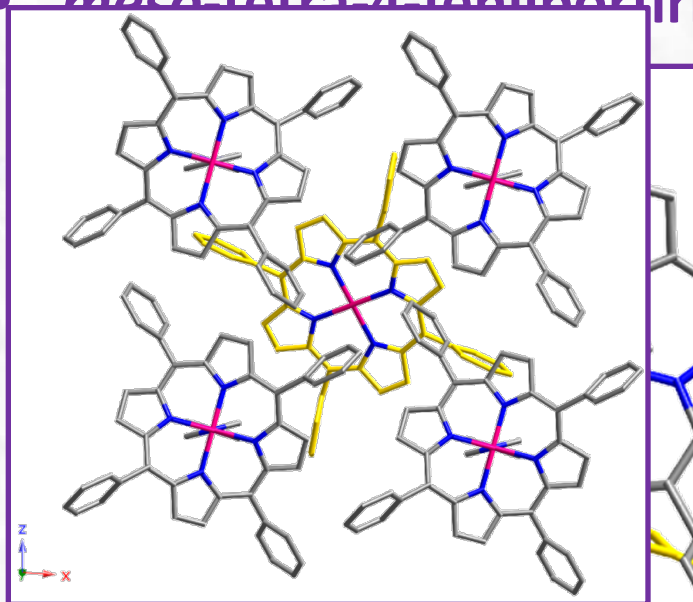
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• *meso*-tetra-4-fenilporfirina (TPP)



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- SGIker por las medidas realizadas y el apoyo mostrado

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Muchas gracias

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