



# MOFs metaloporfirínicos: biomimetizando sus propiedades naturales

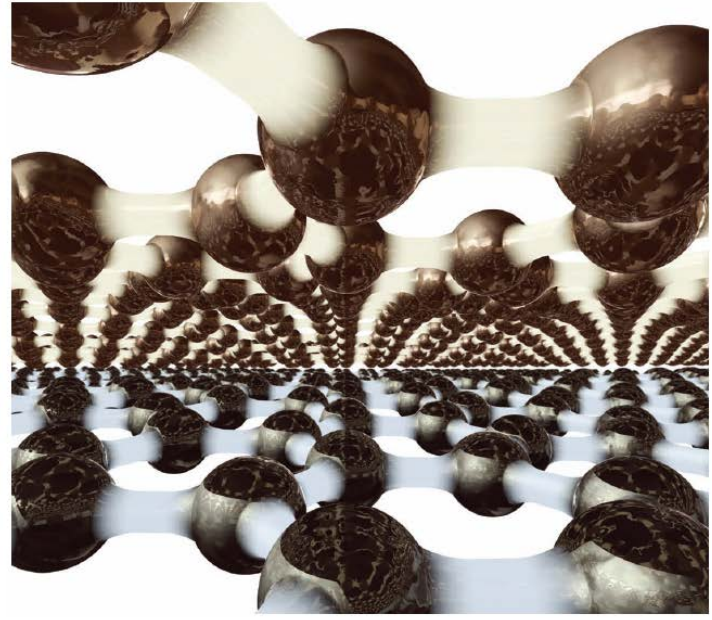
Arkaitz Fidalgo-Marijuan<sup>1</sup>, Eder Amayuelas<sup>1</sup>, Gotzone Barandika<sup>2</sup>, Begoña Bazán<sup>1,3</sup>, Miren Karmele Urriaga<sup>1</sup>, Edurne S. Larrea<sup>1</sup>, Marta Iglesias<sup>4</sup>, Maria Isabel Arriortua<sup>1,3</sup>

<sup>1</sup>Departamento de Mineralogía y Petrología y <sup>2</sup>Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Leioa, Bizkaia

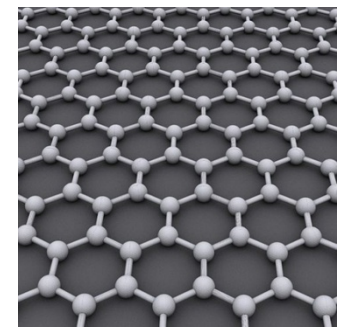
<sup>3</sup>BCMaterials, Basque Center for Materials, Applications and Nanostructures, Parque Tecnológico de Zamudio, Derio, Bizkaia

<sup>4</sup>Instituto de Ciencia de Materiales de Madrid-CSIC, Cantoblanco, Madrid

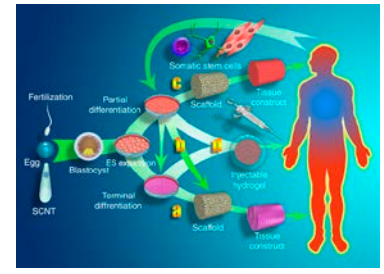
# LINEAS PRIORITARIAS



## 1) Grafeno



## 2) Biomateriales



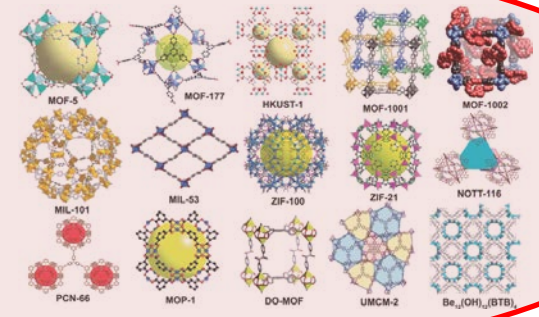
GLOBAL RESEARCH REPORT  
**MATERIALS SCIENCE  
AND TECHNOLOGY**

JUNE 2011  
JONATHAN ADAMS  
DAVID PENDLEBURY

EVIDENCE



## 3) MOFs

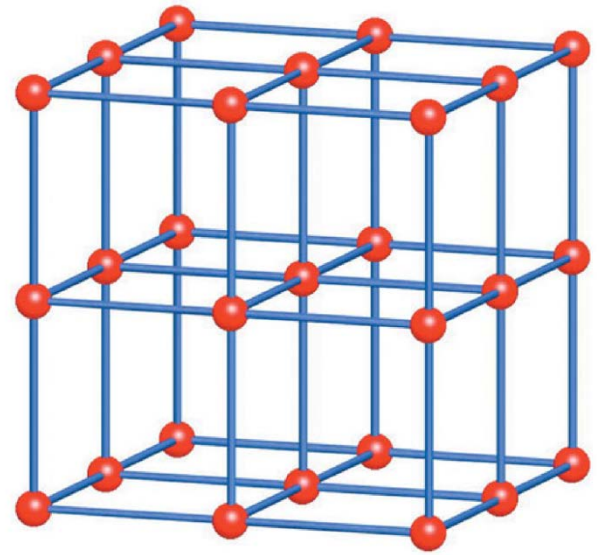
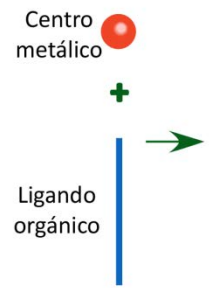


# MOFs

Adsorbentes (H<sub>2</sub>, CO<sub>2</sub>...)

Catalizadores heterogéneos

Liberación fármacos



Conductividad

Ferroelectricidad

Optoelectrónica

Magnetismo

Luminiscencia

## MOFs Metal-Organic Frameworks

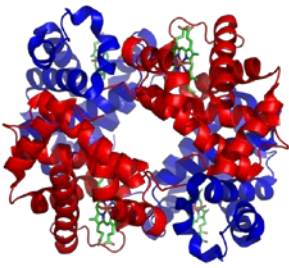


-Gao, C., *Nature* **2013**, 494, 404.

-Adams, J.; Pendlebury, D., *Global Research Report. Materials Science and Technology*. In Thomson Reuters: Junio 2011



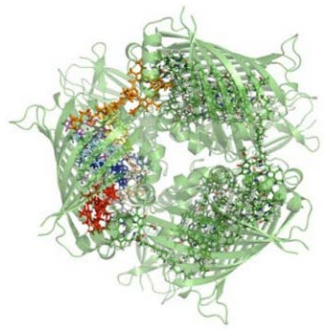
# PORFIRINAS



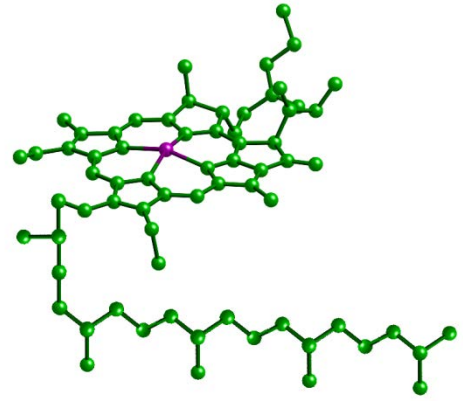
Hemoglobina



Transporte O<sub>2</sub>



Clorofila

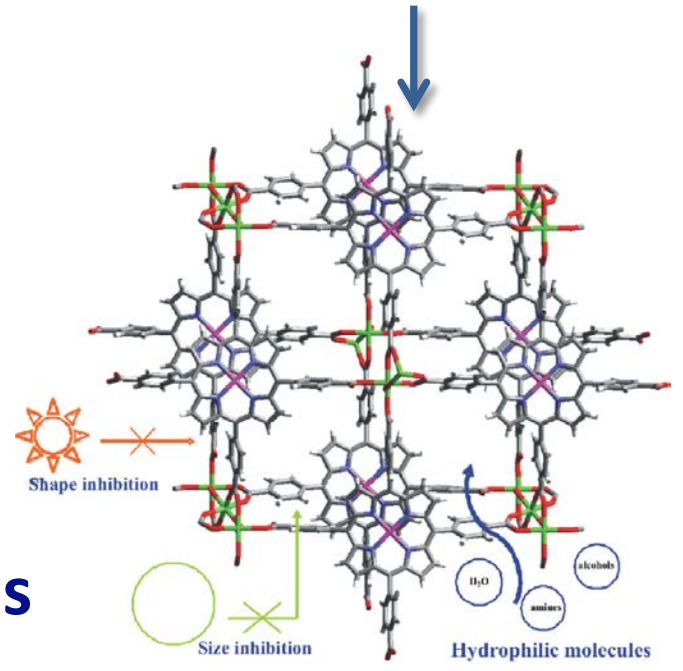


Fotosíntesis

Transferencia de:

- moléculas
- iones
- electrones
- fotones

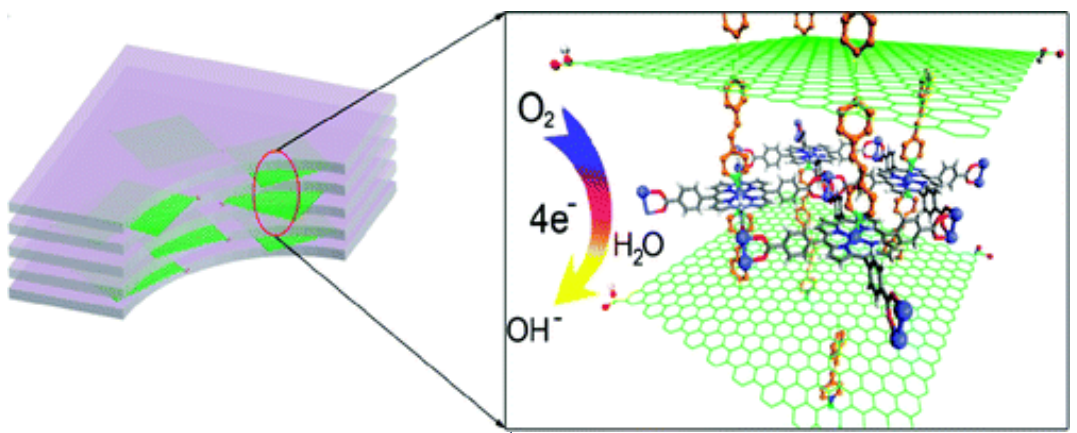
## Mimetismo



## Catalizadores heterogéneos

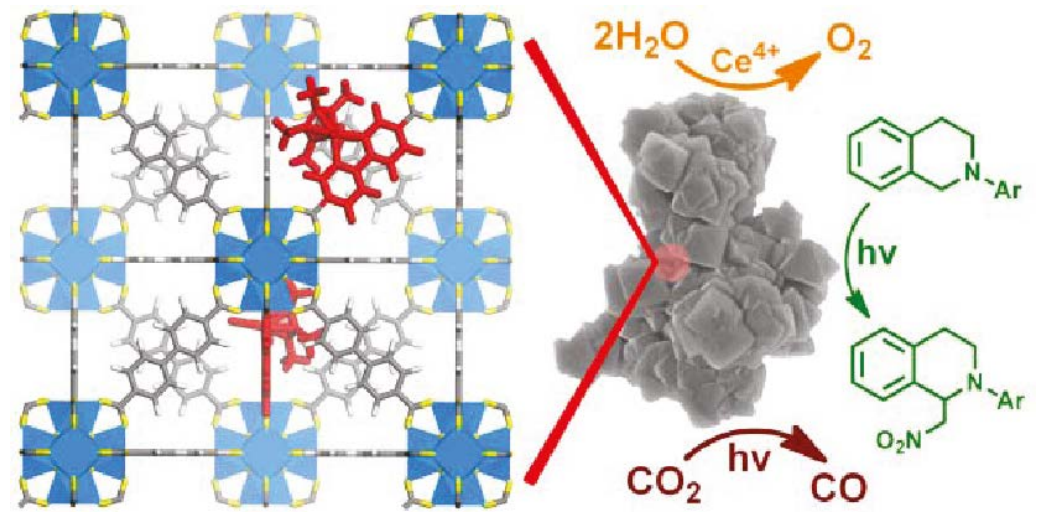
-Reutilizar catalizador





Anclaje de porfirinas en superficies

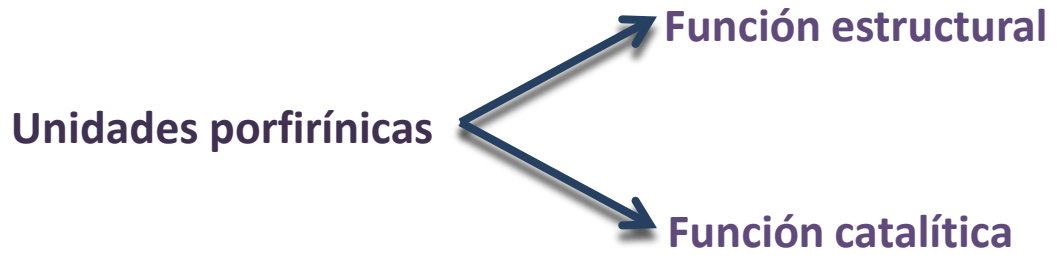
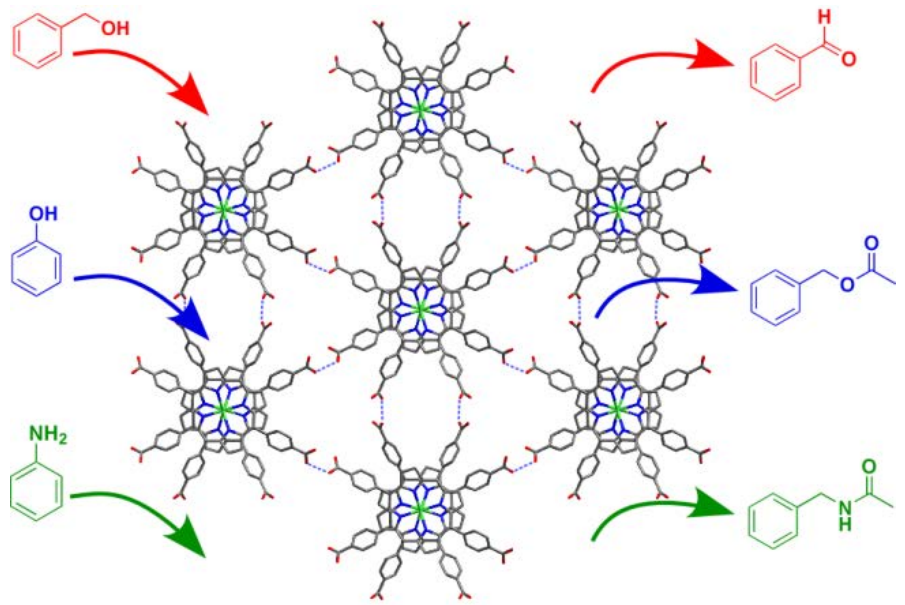
Dopar MOFs porosos

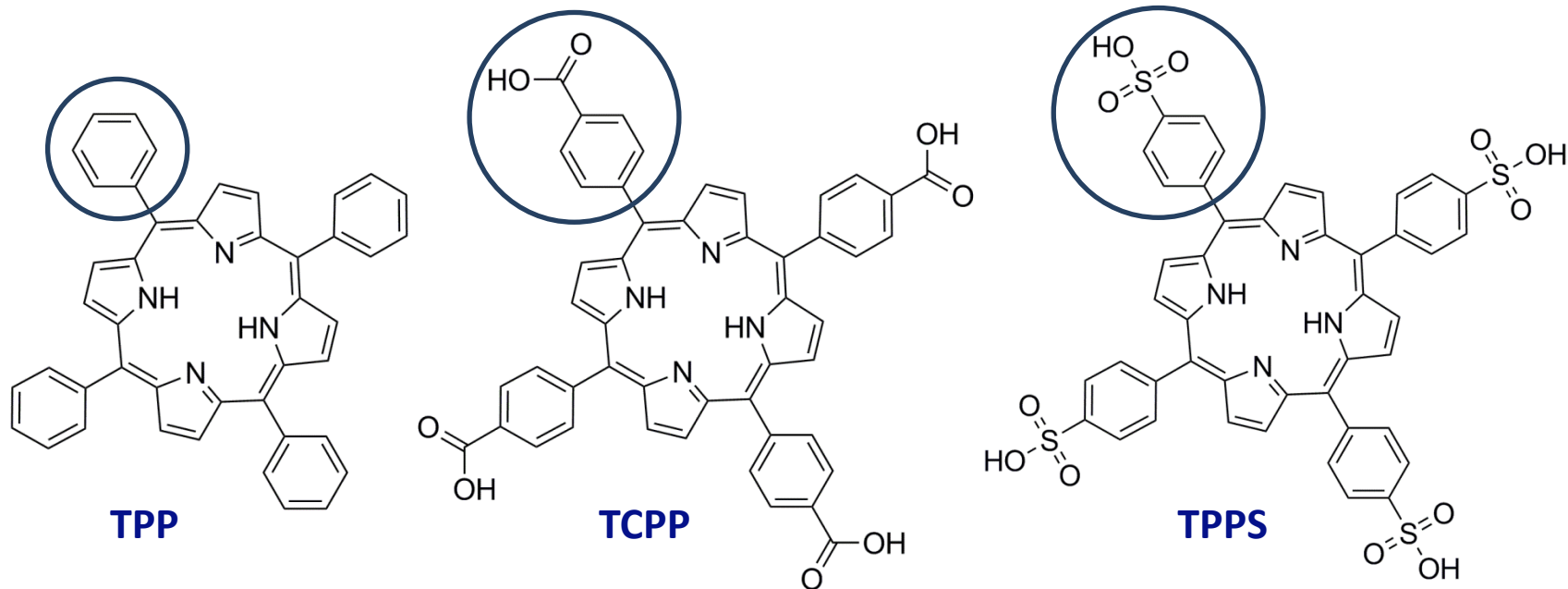


- Jahan, M.; Bao, Q.; Loh, K. P., *J. Am. Chem. Soc.* **2012**, *134*, 6707.  
 - Wang, C.; Xie, Z.; deKrafft, K. E.; Lin, W., *J. Am. Chem. Soc.* **2011**, *133*, 13445-13454.

Estrategias novedosa:

- MOFs porfirínicos con actividad catalítica





**Fe<sup>III</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Mn<sup>II</sup>, Mn<sup>III</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>**

**TPP** = *meso*-tetra-4-fenilporfirina

**TCPP** = *meso*-tetra-4-carboxifenilporfirina

**TPPS** = *meso*-tetra-4-sulfonatofenilporfirina



## ESTRUCTURAS EN LA CSD

	TPP	TCPP	TPPS
Fe	273	12	
Co	82	8	1
Mn	119	14	
Cu	14	10	1
Ni	7	12	

Número de estructuras en la Cambridge Structural Database (CSD)





## NUEVAS ESTRUCTURAS

### 4 Unidades monoméricas o diméricas (0D)

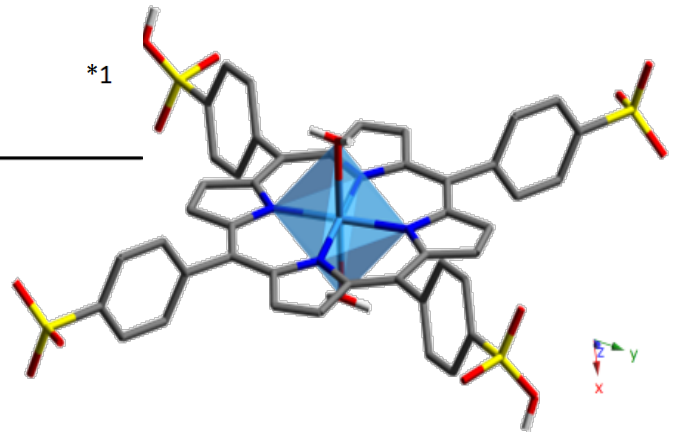
	TPP	TCP	TPPS
Fe	1 *273	2 *12	1 ←
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2 ←
Cu	*14	1 *10	*1
Ni	*7	1 *12	

\*Número de estructuras en la Cambridge Structural Database (CSD)

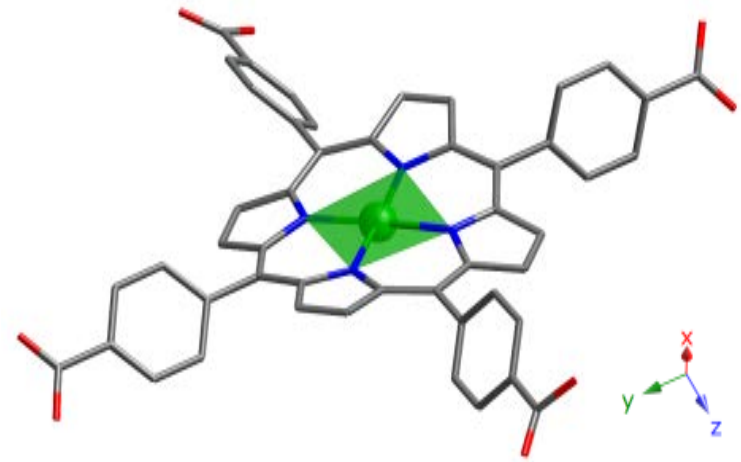
-Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Larrea, E. S.; Iglesias, M.; Lezama, L.; Arriortua, M. I., *Dalton Trans.* **2015**, 44, 213-222.

	TPP	TCPP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

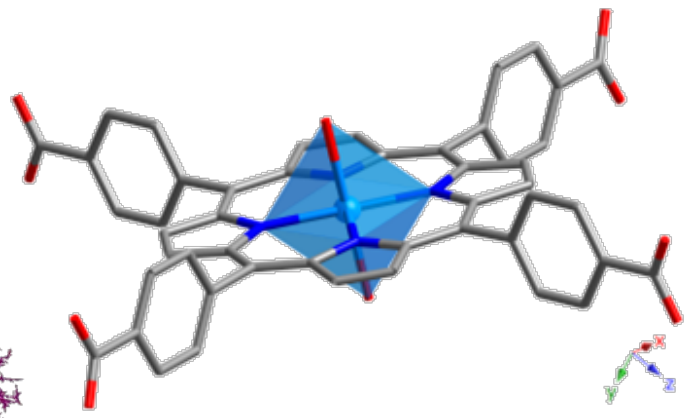
4 Unidades monoméricas o diméricas (0D)



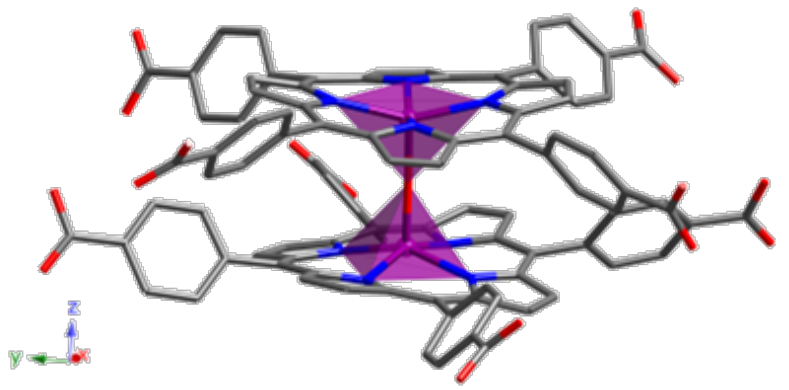
$H(bipy)_2[MnTPPS_{0.5}(H_2O)] \cdot 7(H_2O)$



$[CuTCPP] \cdot 6DMF$



$[Mn(TCPP)(H_2O)_2] \cdot nEtOH$



$\mu-O-[FeTCPP]_2 \cdot 16DMF$



## NUEVAS ESTRUCTURAS

### 4 Unidades monoméricas o diméricas (0D)

### 3 Cadenas (1D)

	TPP	TCP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

\*Número de estructuras en la Cambridge Structural Database (CSD)

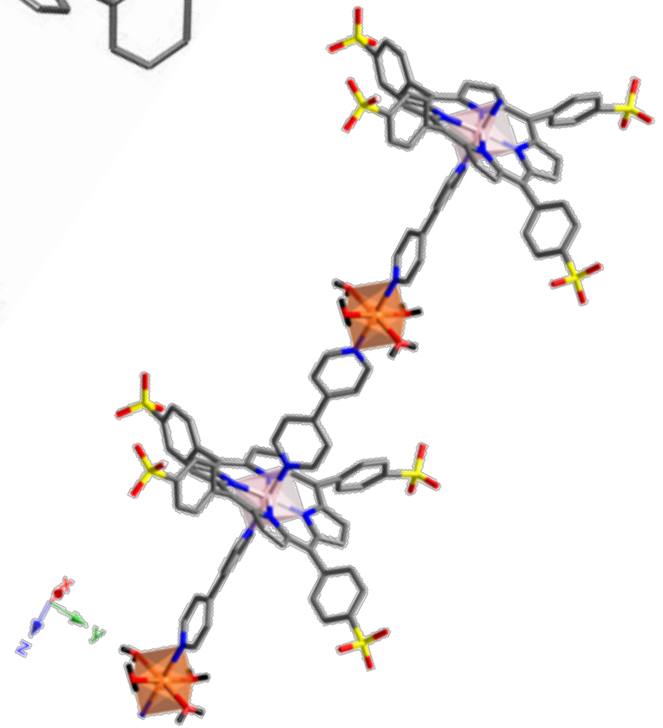
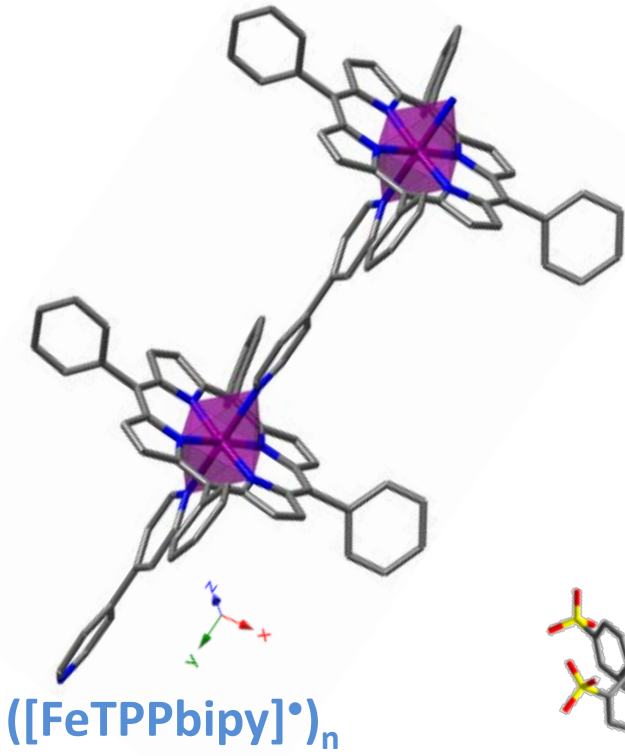
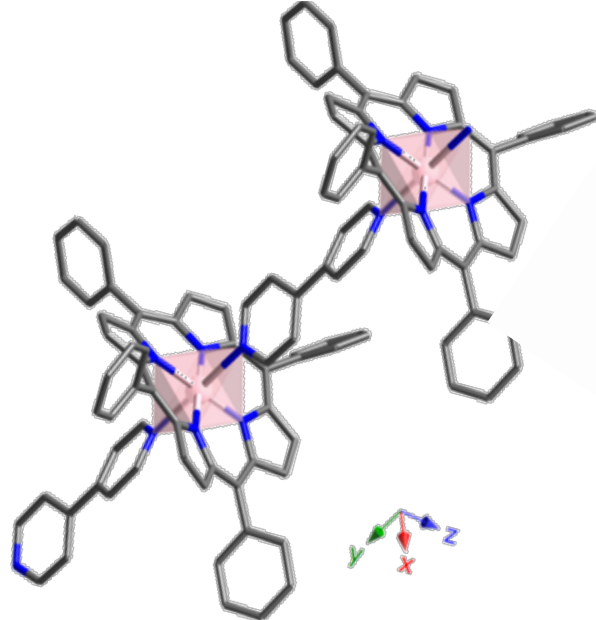
-Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Larrea, E. S.; Iglesias, M.; Lezama, L.; Arriortua, M. I., *Dalton Trans.* **2015**, 44, 213-222.

- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Lezama, L.; Arriortua, M. I., *Inorg. Chem.* **2013**, 52, 8074-8081.

- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *CrystEngComm* **2013**, 15, 4181-4188.

	TPP	TCPP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

3 Cadenas (1D)





## NUEVAS ESTRUCTURAS

4 Unidades monoméricas  
o diméricas (0D)

3 Cadenas (1D)

4 Estructuras laminares (2D)

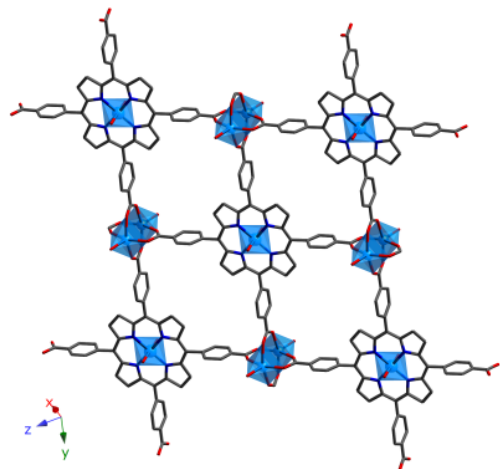
	TPP	TCP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

\*Número de estructuras en la Cambridge Structural Database (CSD)

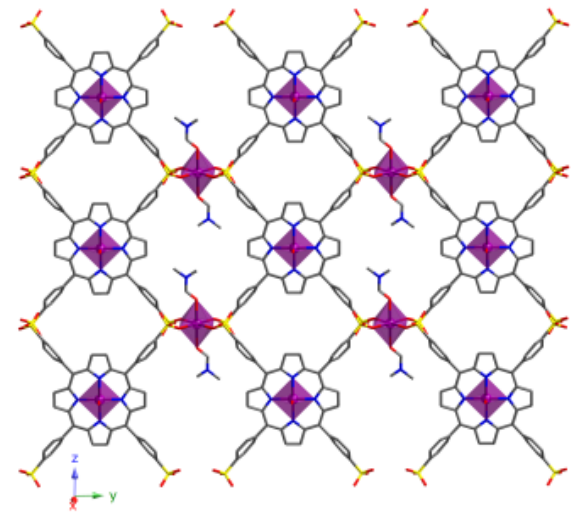
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Larrea, E. S.; Iglesias, M.; Lezama, L.; Arriortua, M. I., *Dalton Trans.* **2015**, 44, 213-222.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Lezama, L.; Arriortua, M. I., *Inorg. Chem.* **2013**, 52, 8074-8081.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *CrystEngComm* **2013**, 15, 4181-4188.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *Polyhedron* **2011**, 30, 2711-2716.

	TPP	TCPP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

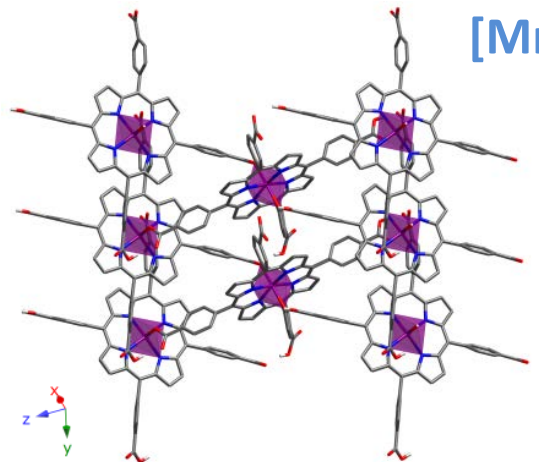
4 Estructuras laminares (2D)



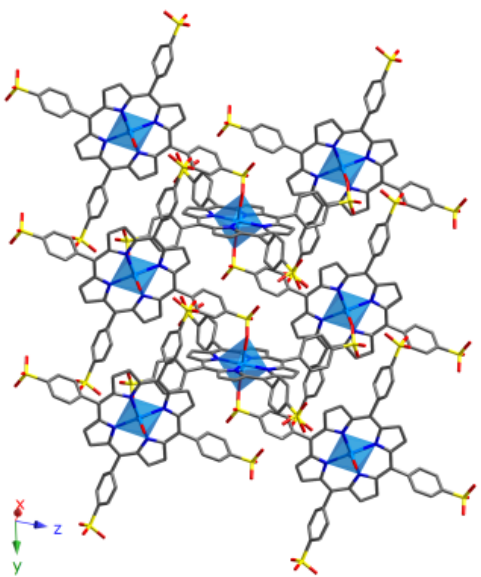
$[Mn_3(TCPP)(H_2O)_4] \cdot EtOH \cdot 2DMF$



$[Fe_2TPPS(DMF)_2(H_2O)_2] \cdot DMF$



$[FeTCPP]$



$[MnTPPS] \cdot 3DMF$



## NUEVAS ESTRUCTURAS

4 Unidades monoméricas  
o diméricas (0D)

3 Cadenas (1D)

4 Estructuras laminares (2D)

1 Estructura  
tridimensional (3D)

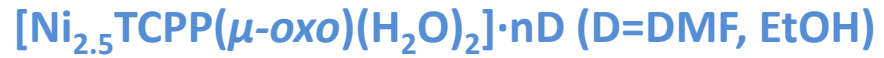
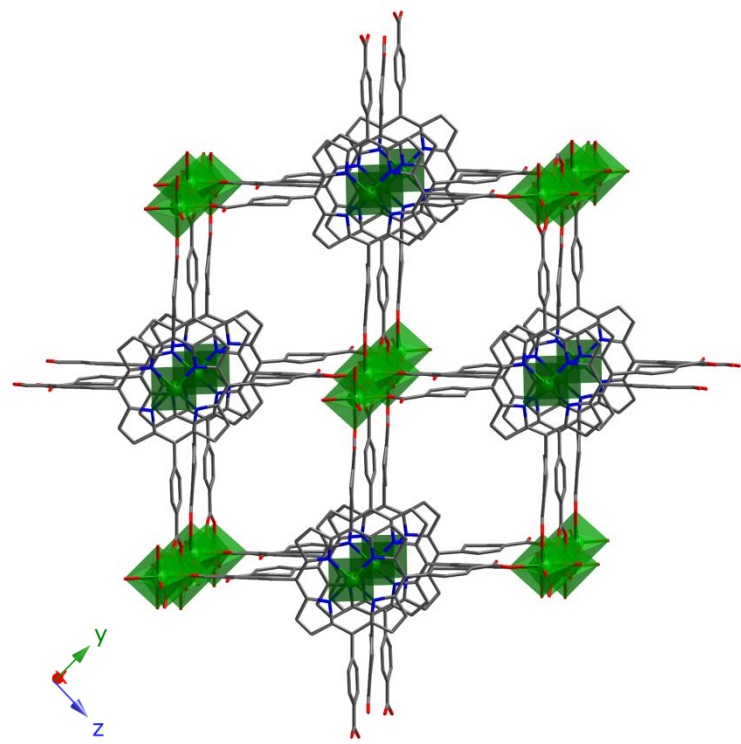
	TPP	TCP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

\*Número de estructuras en la Cambridge Structural Database (CSD)

- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Larrea, E. S.; Iglesias, M.; Lezama, L.; Arriortua, M. I., *Dalton Trans.* **2015**, 44, 213-222.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Lezama, L.; Arriortua, M. I., *Inorg. Chem.* **2013**, 52, 8074-8081.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *CrystEngComm* **2013**, 15, 4181-4188.
- Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *Polyhedron* **2011**, 30, 2711-2716.
- Fidalgo-Marijuan, A.; Amayuelas, E.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Arriortua, M. I., *Molecules* **2015**, 20, 6683-6699.

	TPP	TCPP	TPPS
Fe	1 *273	2 *12	1
Co	1 *82	*8	1 *1
Mn	*119	2 *14	2
Cu	*14	1 *10	*1
Ni	*7	1 *12	

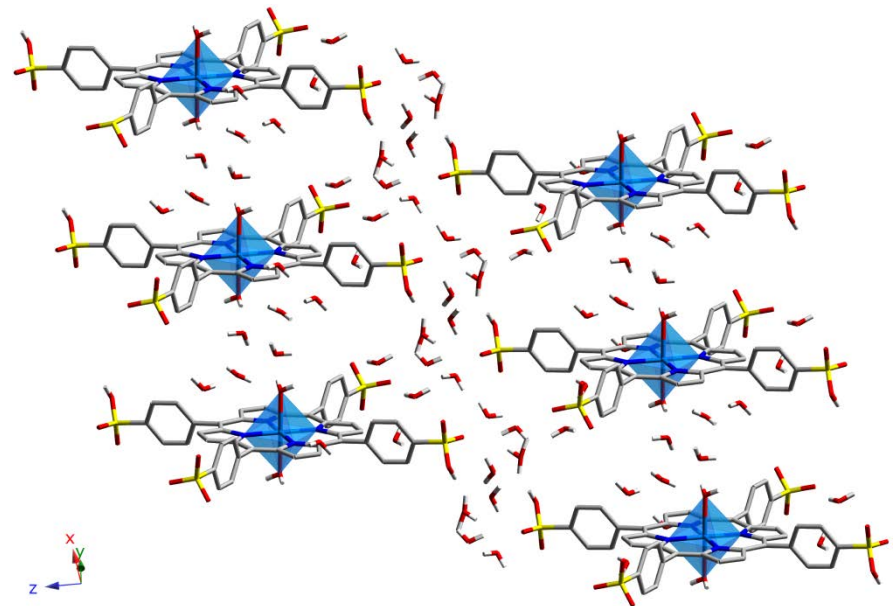
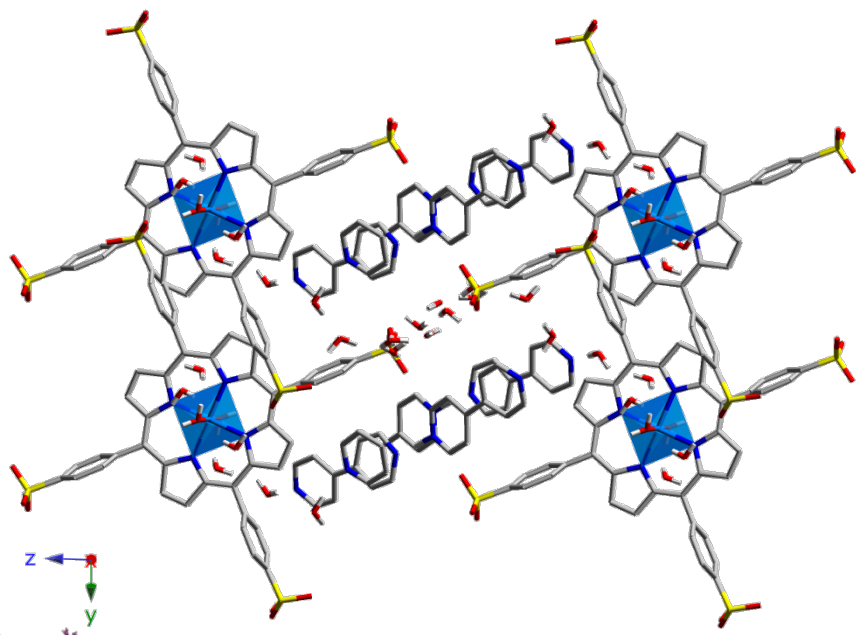
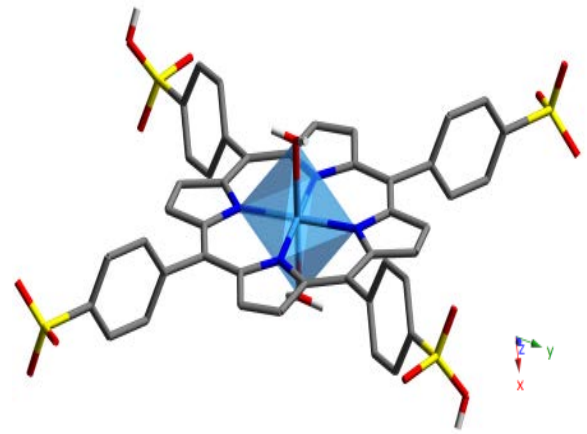
### 1 Estructura tridimensional (3D)





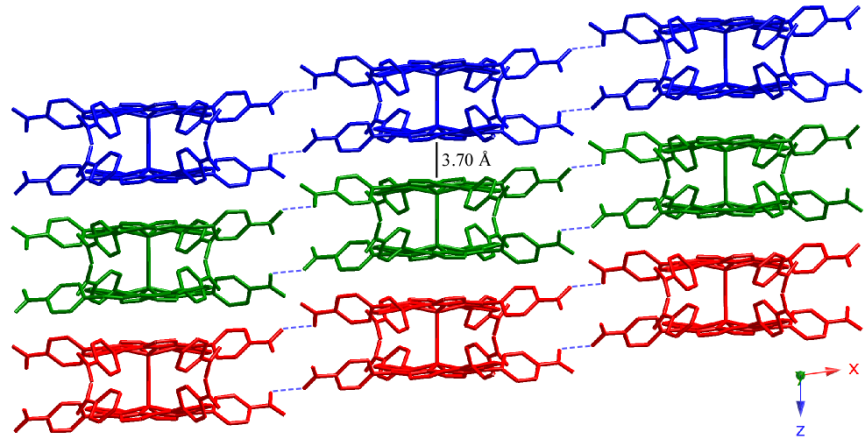
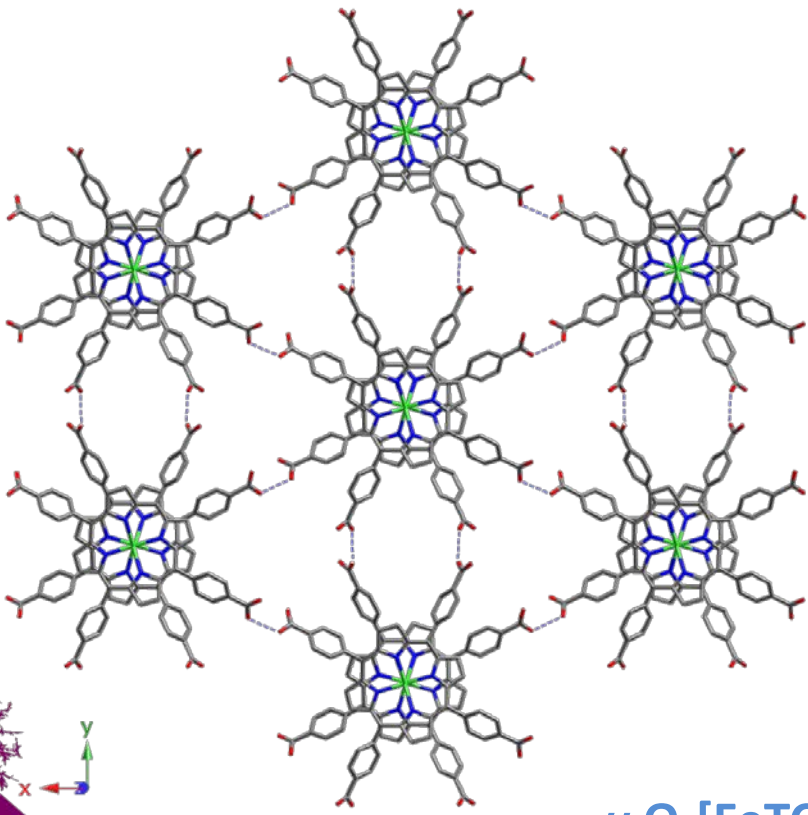
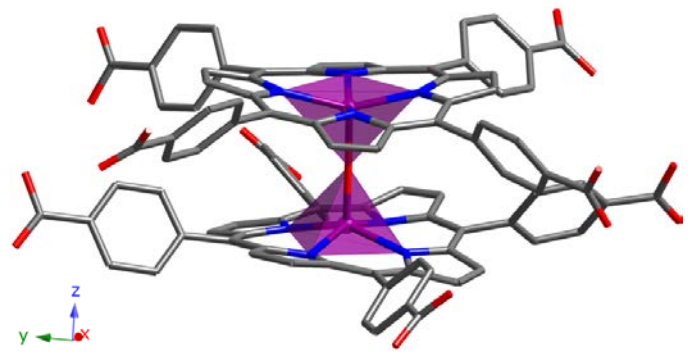
# ESTRUCTURAS SELECCIONADAS

- Variedad en los centros metálicos (Mn, Fe y Co)
- Accesibilidad a moléculas externas
- Centro metálico expuesto al poro



# ESTRUCTURAS SELECCIONADAS

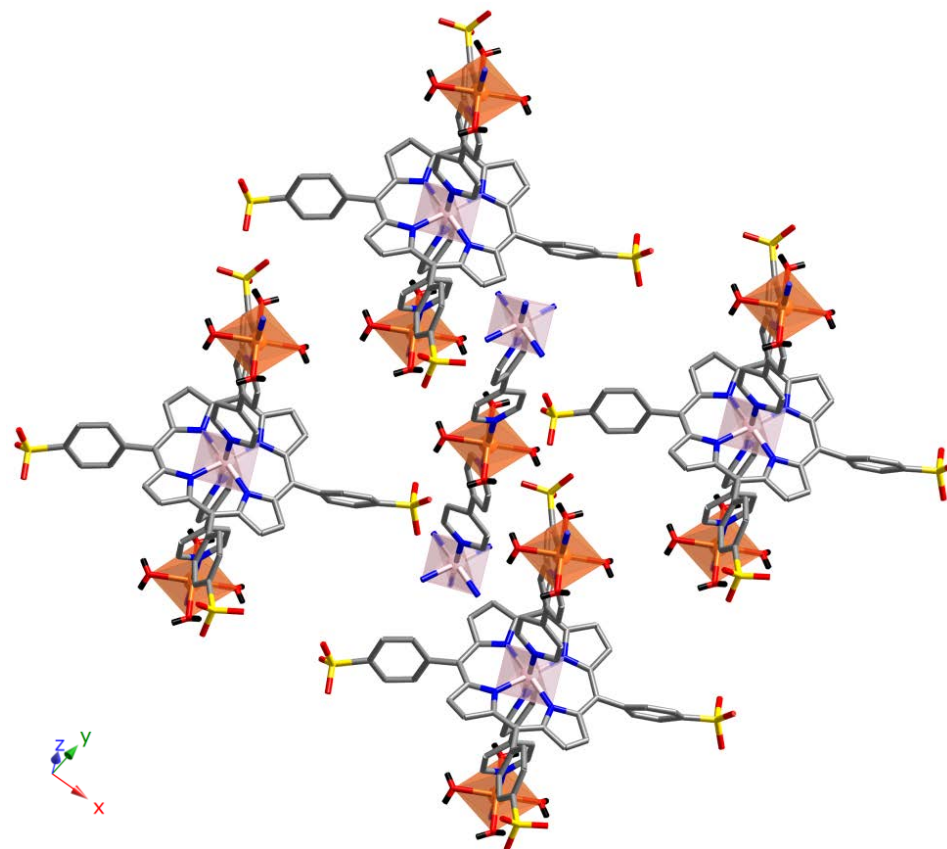
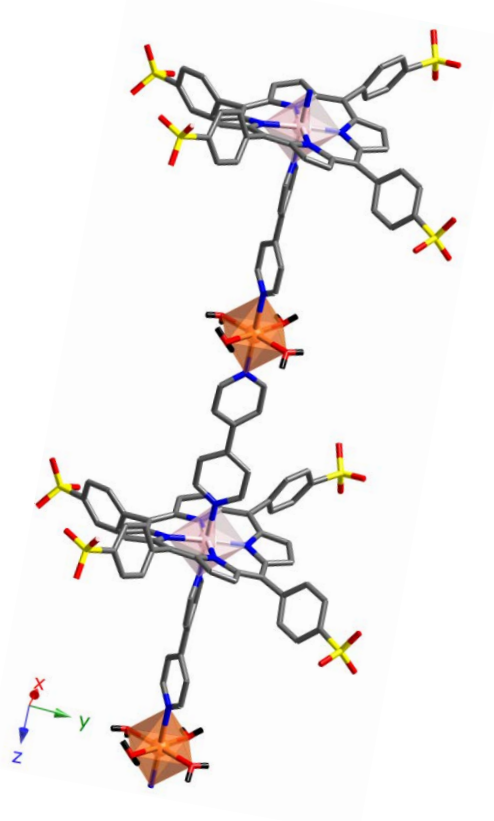
- Variedad de centros metálicos (Mn, Fe y Co)
- Accesibilidad a moléculas externas
- Centro metálico expuesto al poro



$\mu\text{-O-}[\text{FeTCPP}]_2 \cdot 16\text{DMF}$

## ESTRUCTURAS SELECCIONADAS

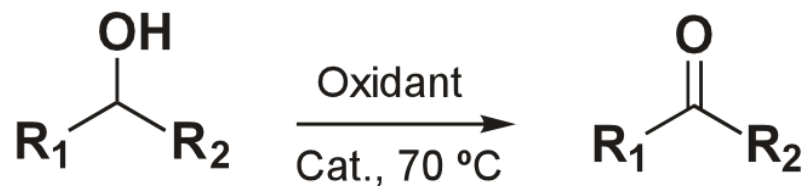
- Variedad en los centros metálicos (Mn, Fe y Co)
- Accesibilidad a moléculas externas
- Centro metálico expuesto al poro



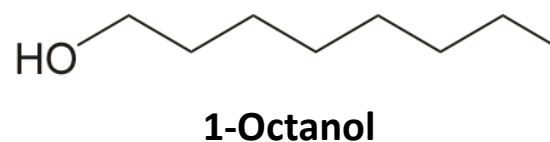
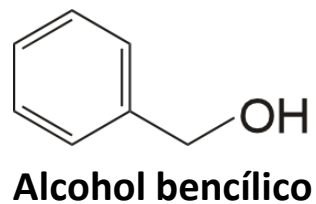
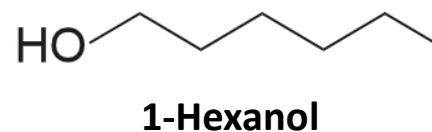
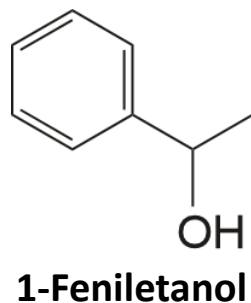


## ACTIVIDAD CATALÍTICA

### Oxidación de alcoholes

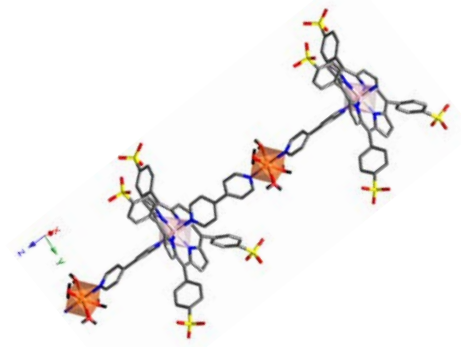
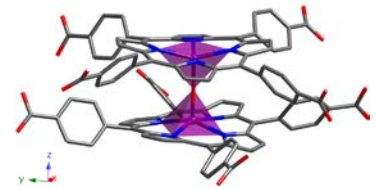
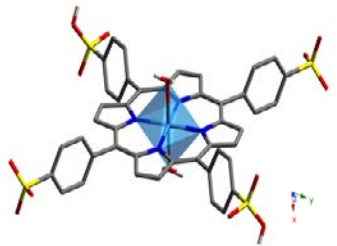


### Sustratos

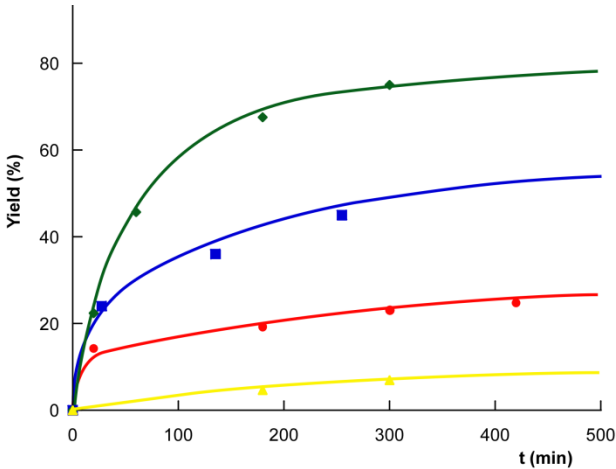


# ACTIVIDAD CATALÍTICA

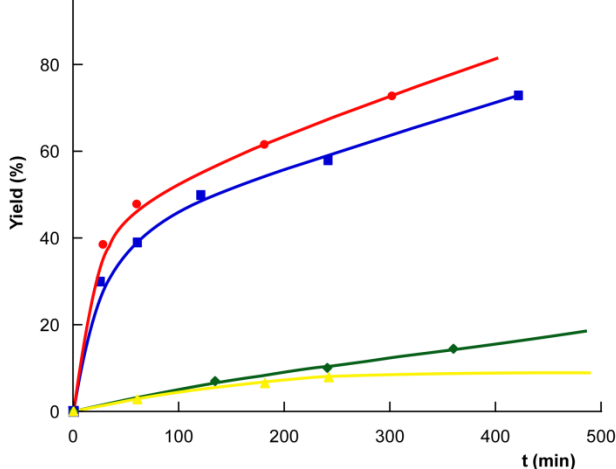
## Resultados



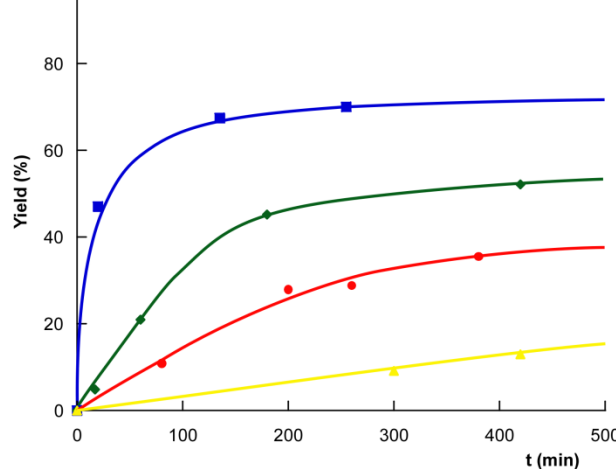
???[MnTPPS<sub>0.5</sub>(H<sub>2</sub>O)]·(Hbipy)·(bipy)·7(H<sub>2</sub>O)



μ-O-[FeTCPP]<sub>2</sub>·16DMF



[CoTPPS<sub>0.5</sub>(bipy)(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O

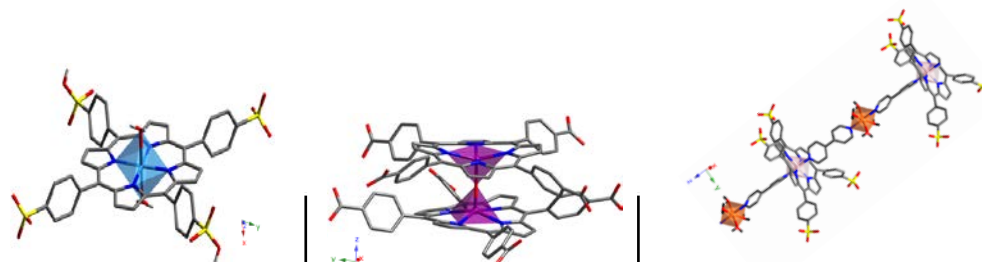


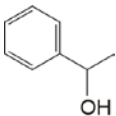
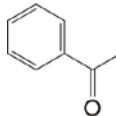
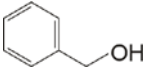
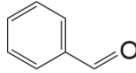


- 1-Feniletanol
- Alcohol bencílico
- ◆ 1-Hexanol
- ▲ 1-Octanol



# ACTIVIDAD CATALÍTICA

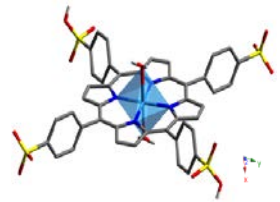
## Resultados



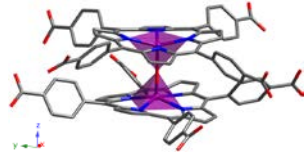
Sustrato	Oxidante	Producto	C <sub>T</sub>	TOF (h <sup>-1</sup> )	C <sub>T</sub>	TOF (h <sup>-1</sup> )	C <sub>T</sub>	TOF (h <sup>-1</sup> )
	TBHP		44	46	<b>73</b>	<b>91</b>	44	8
	TBHP		70	72	73	72	<b>77</b>	<b>143</b>
	TBHP		<b>92</b>	<b>66</b>	15	3	71	22

# ACTIVIDAD CATALÍTICA

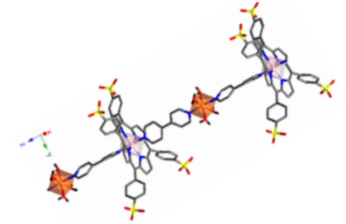
## Resultados



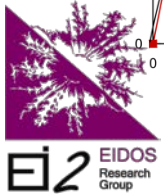
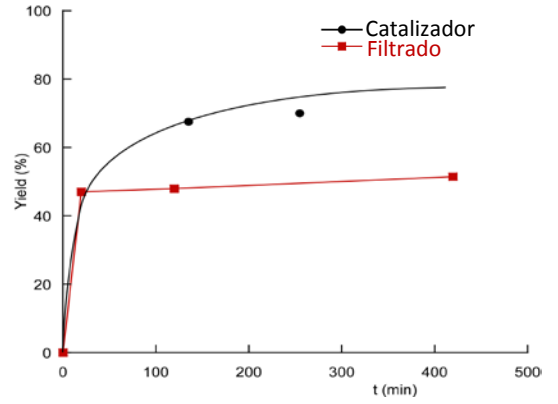
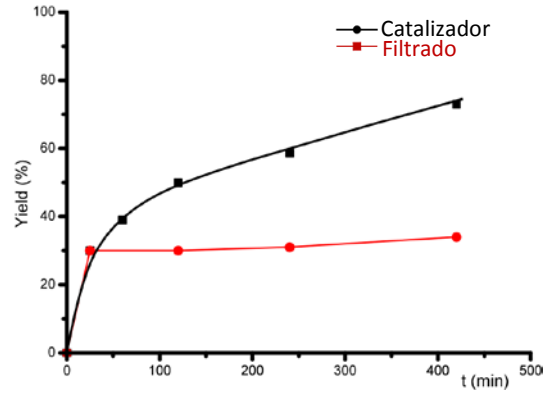
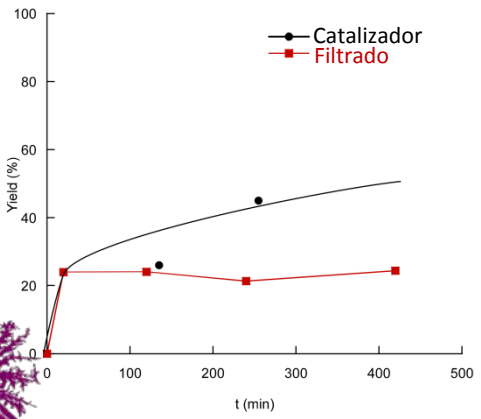
Cycles	C <sub>T</sub> (4h)
1	40%
2	31.3%
3	30.69%
4	26.8%
5	26.4%



Cycles	C <sub>T</sub> (4h)
1	58 %
2	77 %
3	98 %



Cycles	C <sub>T</sub> (4h)
1	27.31
2	31.42
3	32
4	26.8
5	26



## Catalizadores Heterogeneos



## CONCLUSIONES

- MOFs porfirinicos con actividad catalítica heterogenea
- No es tan importante la dimensionalidad del compuesto, como la accesibilidad de la red a los centros activos
- Redes sólidas estabilizadas mediante enlaces de H o interacciones  $\pi$ - $\pi$  presentan una elevada estabilidad térmica



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**Gracias por vuestra  
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