Biomimetic catalysts based on metalloporphyrin MOFs

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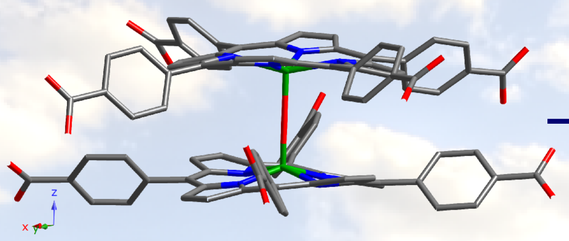
Introduction

During the past years, a great effort has been devoted to the anchoring of catalysts into MOFs in order to achieve heterogeneous catalysts [1]. In this sense, an innovative approach consists on using metalloporphyrins as coordination-network synthons mimicking their natural catalytic activity in order to reproduce it in the solid state [2].

The work herein presented explores the activity of μ-O-[FeTCPP]$_2$·nDMF (TCPP= *meso*-tetracarboxyphenylporphyrin; n=16) and [CoTPPS$_{0.5}$(bipy)(H$_2$O)$_2$]·6H$_2$O [3] (TPPS= *meso*-tetrasulfonatophenylporphyrin, bipy= 4,4´-bipyridine) compounds as heterogeneous catalysts on oxidation reactions of different organic substrates [4].

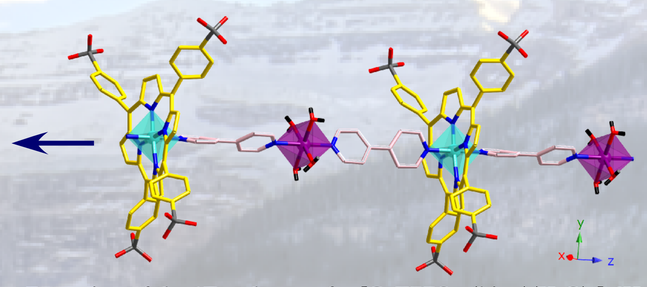
Crystal structures



Dimeric unit for [FeTCPP]$_2$O ·nDMF.
Colour code: Fe=green, N=blue, C=black and O=red

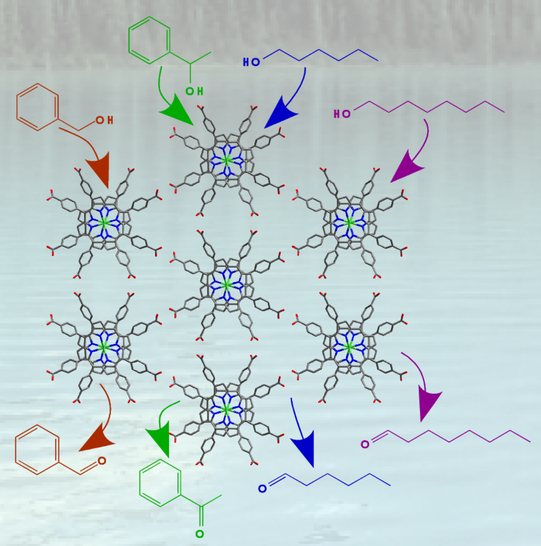
Empirical formula	$C_{96}H_{52}Fe_2N_8O_{17}$
Formula Weight	1701.16 g/mol
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell dimensions	*a*=39.3340(4) Å
	b=19.8329(2) Å
	c=16.0292(2) Å
	β=98.418(1)°
Volume	12369.8(2) Å^3
Z, ρ_{calc}, ρ_{obs}	4, 0.911, 1.575(5) g/cm^3
Final R indexes	R_1=0.0609, wR_2=0.1869

Empirical formula	$C_{32}H_{36}CoN_4O_{14}S_2$
Formula weigth	811.62 g/mol
Crystal system	Tetragonal
Space group	*I* 4$_1$/*a*
Cell dimensions	*a*=17.9776(2) Å
	c=22.3657(3) Å
Volume	7225.55(15) Å^3
Z, ρ_{calc}, ρ_{obs}	8, 1.492, 1.488(4) g/cm^3
Final R indexes	R_1=0.0669, wR_2=0.1845

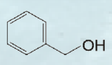
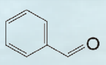
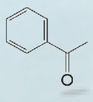


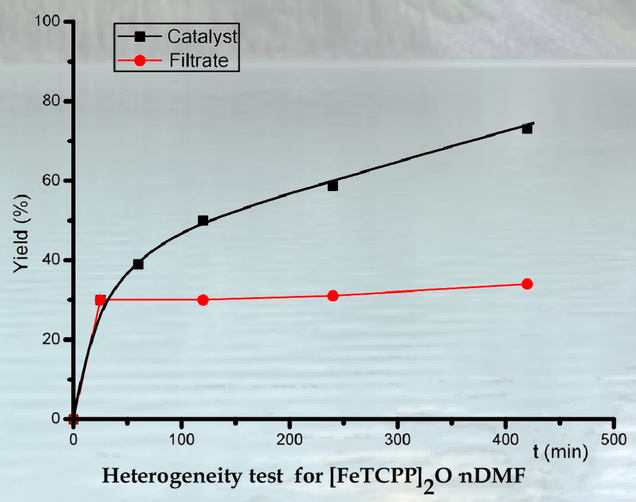
Extension of the 1D polymers for [CoTPPS$_{0.5}$(bipy)(H$_2$O)$_2$]·6H$_2$O.
Colour code: Co(1) (TPPS)=turquoise, Co(2)=purple, N=blue, C (TPPS)=yellow, C (bipy)=pink, O=red, S=grey.

Catalytic Properties

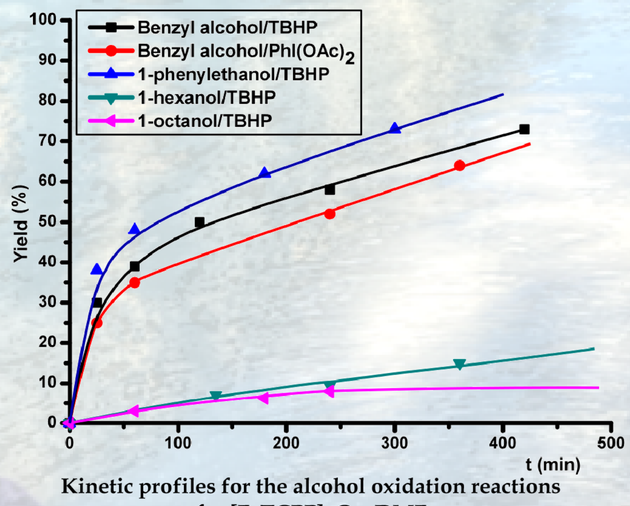


View of the H-bonded 2D layer for [FeTCPP]$_2$O ·nDMF

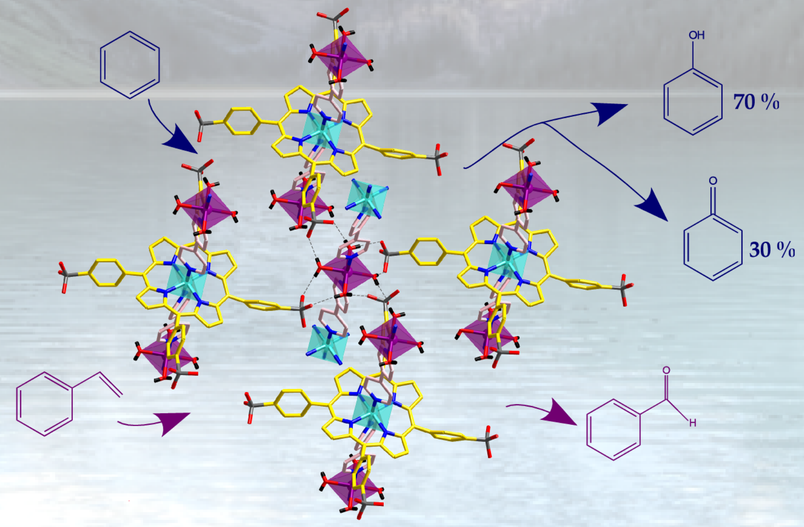
Substrate	Oxidant	Product	TOF (min^{-1})
	TBHP		1.2
	PhI(OAc)$_2$		1.0
	TBHP		1.52
	TBHP		0.05
	TBHP		0.05



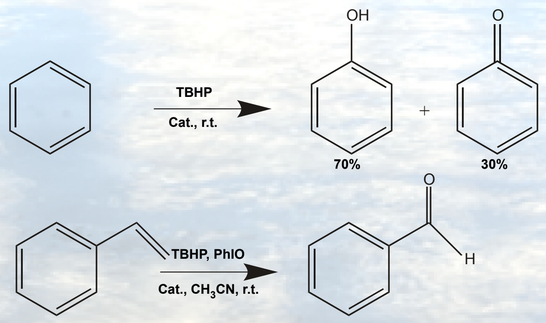
Heterogeneity test for [FeTCPP]$_2$O ·nDMF



Kinetic profiles for the alcohol oxidation reactions for [FeTCPP]$_2$O ·nDMF



View of the H-bonded supramolecular structure for [CoTPPS$_{0.5}$(bipy)(H$_2$O)$_2$]·6H$_2$O.



<u>Oxidants</u>: **TBHP (tert-Butyl hydroperoxide) and PhIO (iodosylbenzene).**

Conclusions

- The metalloporphyrinic structural units of both compounds play as heterogeneous catalysts.
- [FeTCPP]$_2$·nDMF shows excellent catalytic behaviour for different oxidation of alcohols.
- Catalytic tests show that the compound [CoTPPS$_{0.5}$(bipy)(H$_2$O)$_2$]·6H$_2$O exhibits selectivity for the cyclohexane oxidation.

Acknowledgements

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References

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[2] Zhang, Z.; Zhang, L.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M.J., *J. Am. Chem. Soc.*, **2012**, *134*, 928-933.
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