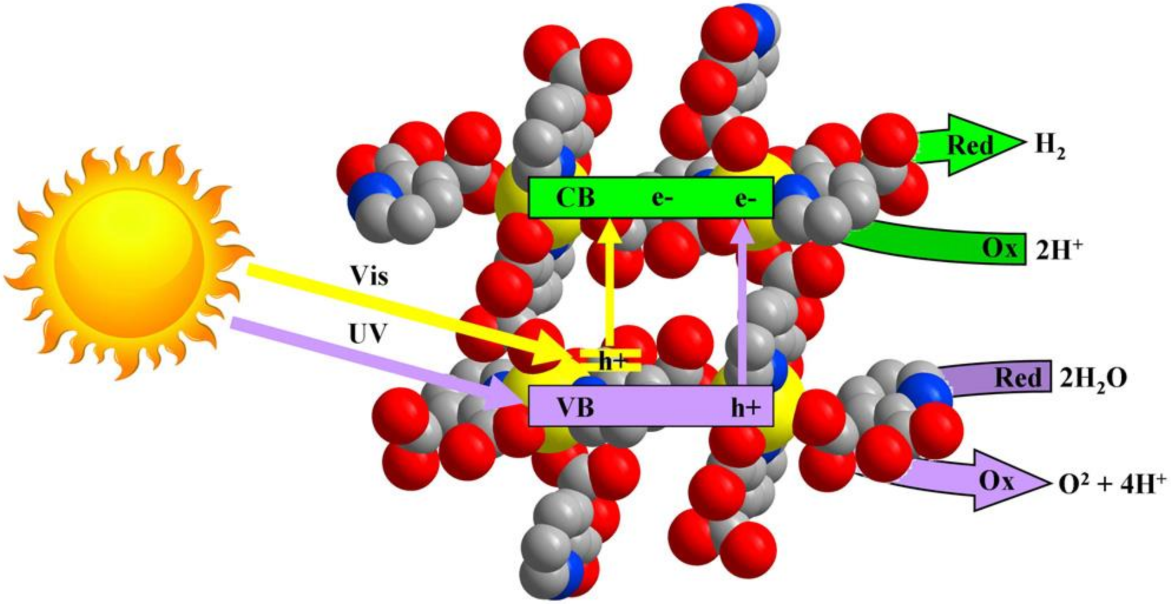
Project Details

Preliminary Registration Code	PD-2016-1708
Final Registration Code	PN-III-P1-1.1-PD-2016-1564
Project Title (Romanian)	Materiale fotocatalitice pentru scindarea apei: de la design la obţinerea de hidrogen utilizând lumina solară
Project Title (English)	Next Level Photocatalytic Materials for Water Splitting: From the Drawing Board to Hydrogen Generation Using Solar Light
Project Acronym	PhotoCatSplit
Contracting Authority	UEFISCDI
Project Host Institution	University of Bucharest
Project Duration / Run Period	26 Months / 10.10.2018 - 30.11.2020
Total Funding	250.000,00 lei

Project Summary

In a world with ever-increasing energy demands, low-cost and clean alternatives of producing fuels are imperiously required. The use of sunlight as a source of free and virtually inexhaustible energy and of water as abundant and attractive raw material indicate that photocatalytic systems sensitive to solar light are a good candidate for hydrogen generation through photocalytic water splitting. However, despite recent progress, transition metal complexes have not yet achieved efficient photocatalytic water splitting, as they rely on sacrificial chemical oxidants or a potential bias. Moreover, turnover numbers and frequencies are not large enough, overpotentials are high, and best catalysts known today do not use earth-abundant elements, but rely on noble metals, therefore being costly and not sustainable.

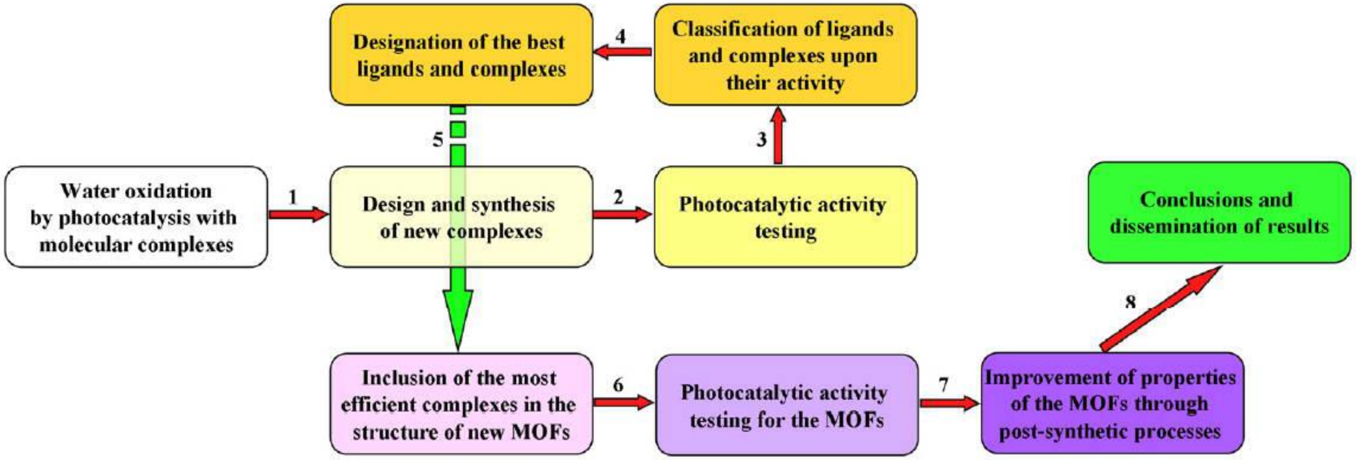


Scheme 1. The principle of action of a photocatalyst for water oxidation

Project Summary

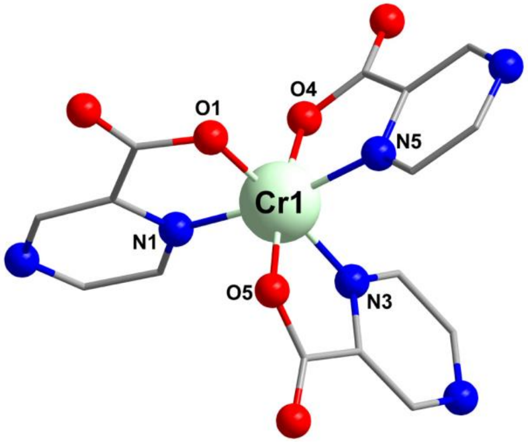
The first part of the project focuses on the synthesis of new complexes containing 3d or 4d metal ions and Schiff-base, polypyridyl derivatives or diketones as ligands, followed by the study of their efficiency in photocatalytic water splitting. The comparison between complexes with $\{M_4O_4\}$ heterocubane core and the $\{Mn_4Ca\}$ oxygen-evolving complex from Photosystem II will help improving the design and photocalytic behaviour of the new materials. Following feed-back from photocatalytic activity testing, the most efficient complexes will be selected.

In the second part of the project, using the novel catalysts as nodes or spacers, new metal-organic frameworks (MOFs) will be obtained and their photocatalytic properties will be determined. MOFs will bring increased catalyst stability and recyclability and will allow a precise tuning of the excitation windows, thus making the new materials better candidates for flow production of hydrogen. The output of this project is represented by new efficient visible-light photocatalysts, which will be the subject of publications in the most relevant high impact factor journals.

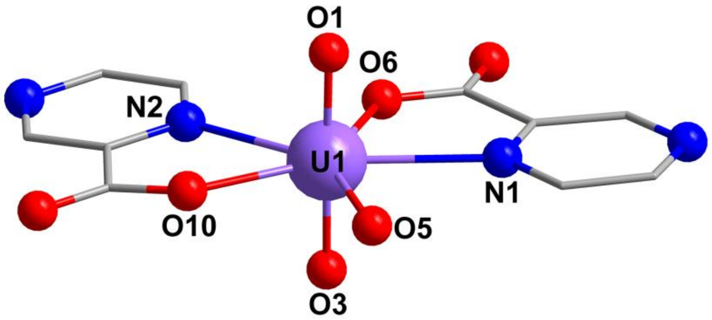


Scheme 2. The flowchart of the project

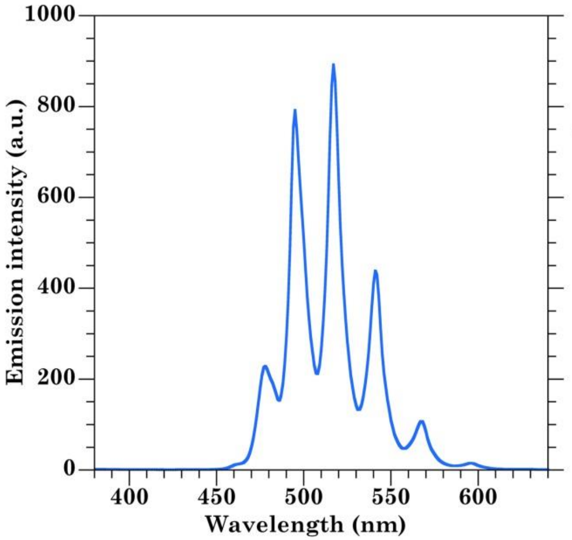
New Metalloligands to be Used as *Building-blocks*

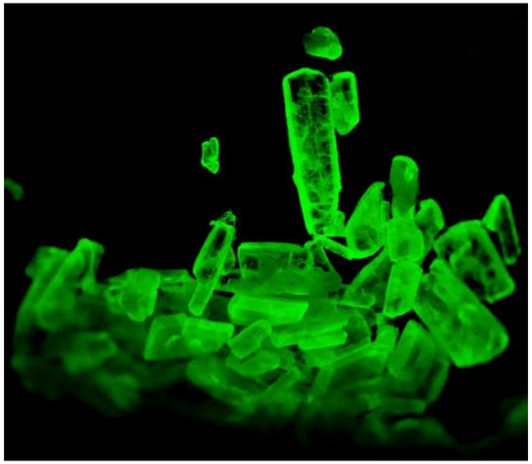


The structure of the $[Cr(pzca)_3]$ complex



The structure of the $[UO_2(pzca)_2(OH_2)_2]$ unit of the $[UO_2(pzca)_2(OH_2)_2]\cdot 2H_2O$complex

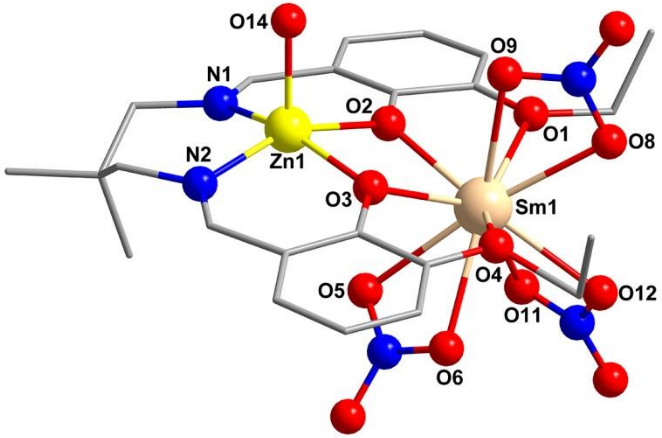




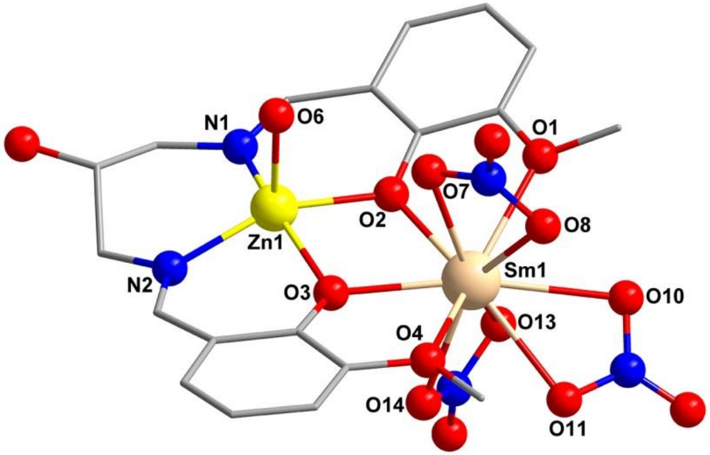
The photoluminescent emission of $[UO_2(pzca)_2(OH_2)_2]\cdot 2H_2O$complex

Traian-Dinu Pasatoiu, Catalin Maxim, Marius Andruh - *Metalloligands Obtained from Pyrazinoic Acid* (poster) –
9th International Conference of the Chemical Societies of the South-East European Countries, Târgovişte, România, 8-11th May 2019

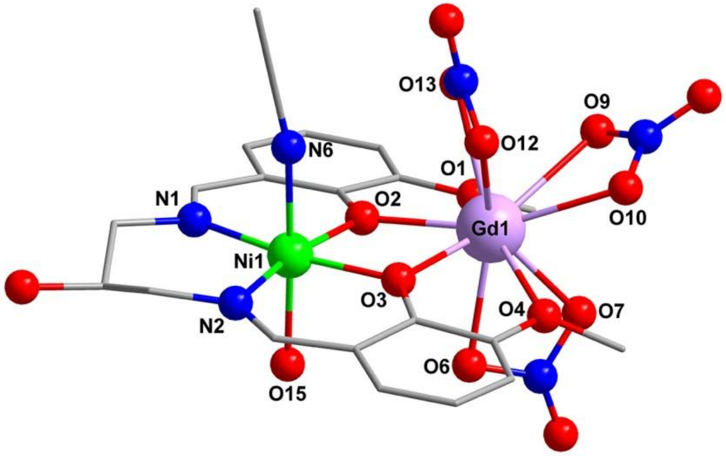
New 3*d*-4*f* *Building-blocks*



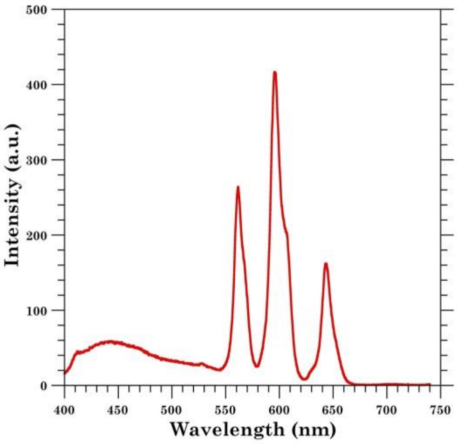
The [$Zn(H_2O)$(esaldmpn)$Sm(O_2NO)_3$] unit



The [$Zn(H_2O)$(valdap)$Sm(O_2NO)_3$] unit



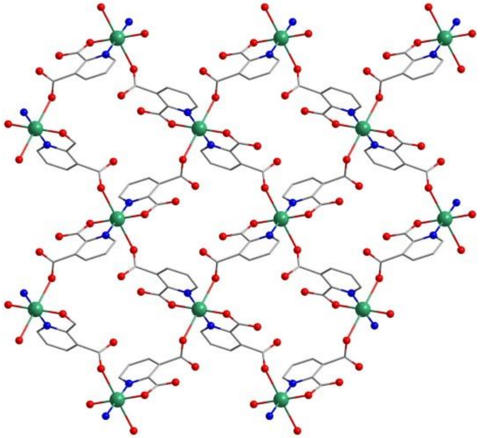
The [$Ni(H_2O)(CH_3CN)$(valdap)$Gd(O_2NO)_3$] unit



The photoluminescent emission of
[$Zn(H_2O)$(valdap)$Sm(O_2NO)_3$]

Traian-Dinu Pasatoiu, Augustin M. Madalan, Marius Andruh - *New Luminescent 3d-4f Building-blocks* (poster) –
9th International Conference of the Chemical Societies of the South-East European Countries, Târgovişte, România, 8-11th May 2019

New Coordination Polymers



The $_{\infty}^{2}$[Cu(2,3-pydca)$_2$] system

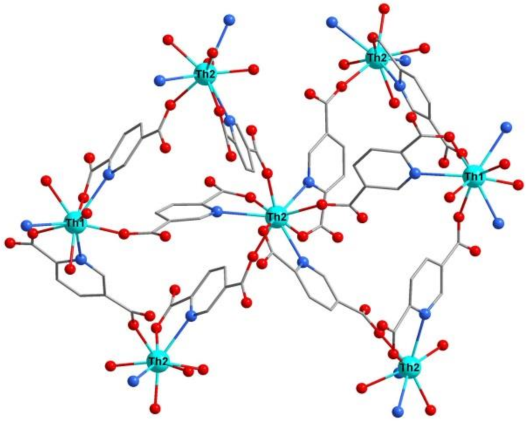
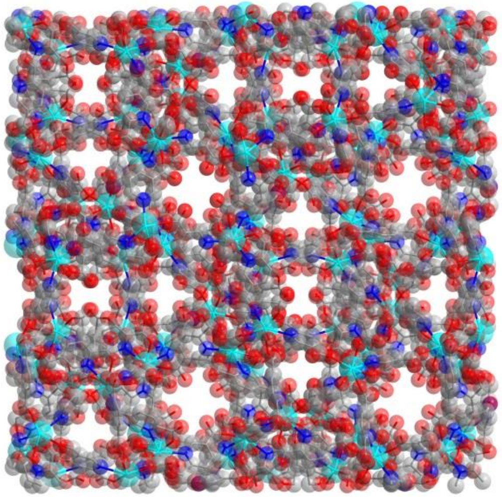


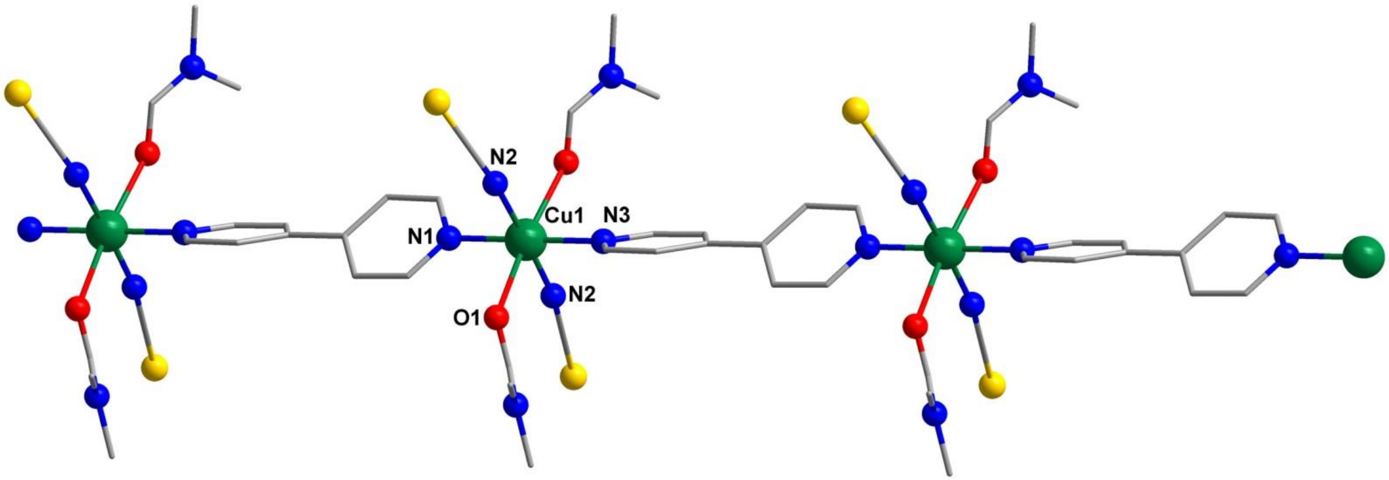
Illustration of the coordination modes of Th(IV) ions in $_{\infty}^{3}$[Th(2,5-pydca)$_3$]



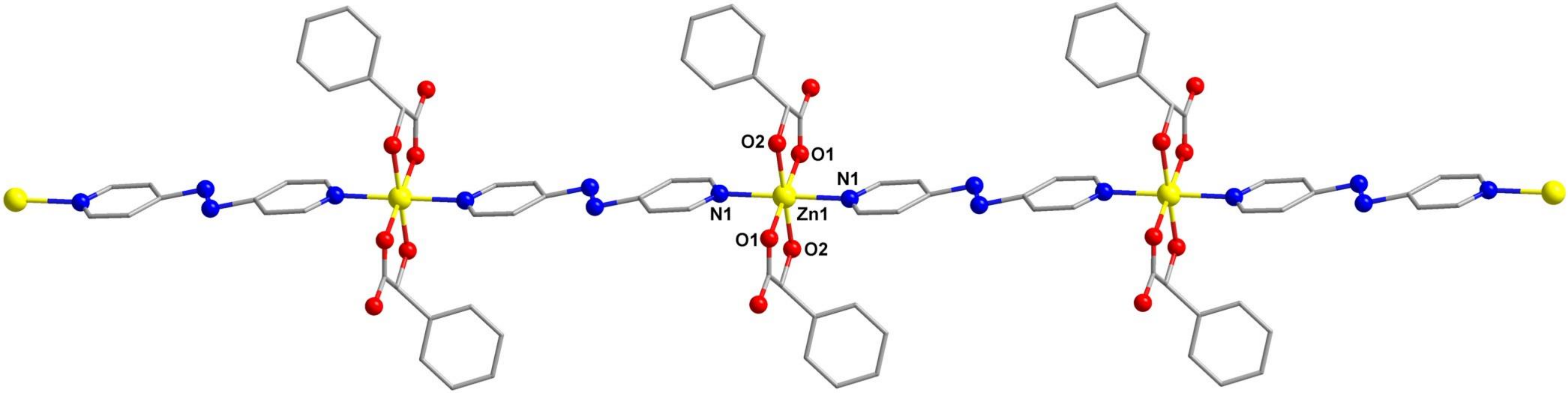
Channels in the solid-state structure of $_{\infty}^{3}$[Th(2,5-pydca)$_3$]

Traian-Dinu Pasatoiu, Catalin Maxim, Marius Andruh - *New Homometallic Systems Obtained Using 3d and 5f Metal Ion Nodes and Carboxylato Spacers* (poster) - 21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE), Mamaia, România, 4-7th September 2019

New Coordination Polymers

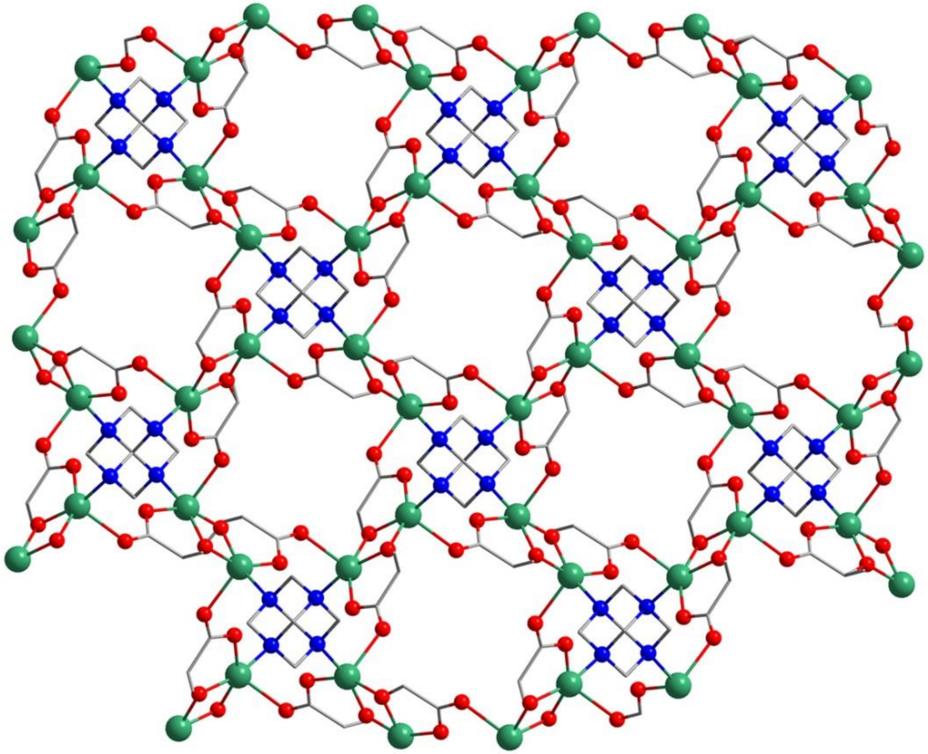


The $_{\infty}^{1}$[Cu(4,4’-bipy)(NCS)$_2$(DMF)] coordination polymer

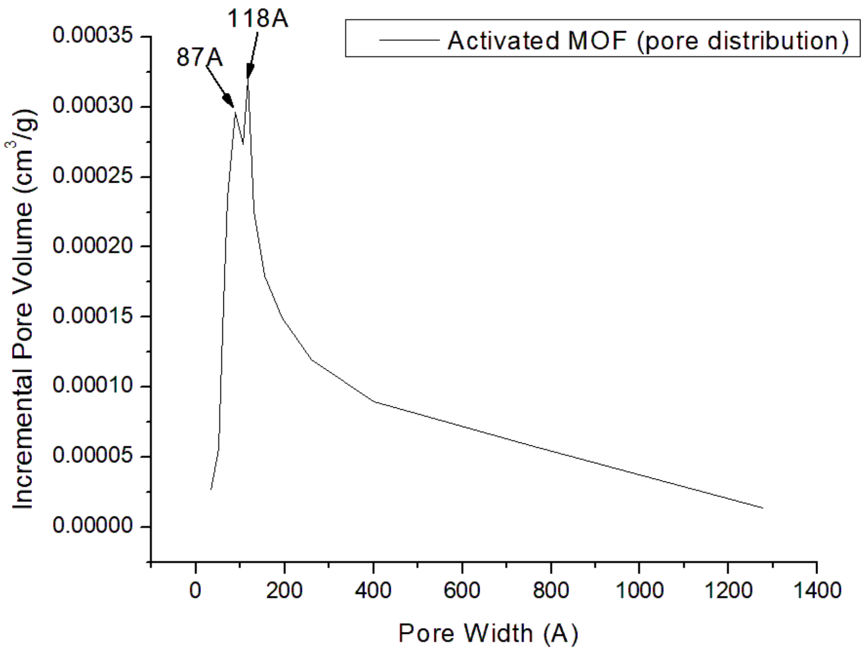


The $_{\infty}^{1}$[Zn(mnd)$_2$(4,4’-azbpy)] coordination polymer

${}_{\infty}^{3}[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction



Solid-state structure of ${}_{\infty}^{3}[Cu_2(mand)_2(hmt)]\bullet H_2O$



Bimodal pore size distribution of the activated MOF

Horatiu Szalad, Natalia Candu, Traian Pasatoiu, Marius Andruh, Vasile Parvulescu - *${}_{\infty}[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction* (poster) - RomCat2019. The 12th International Symposium of the Romanian Catalysis Society, Bucureşti, România, 5-7th June 2019

$_\infty^3[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction

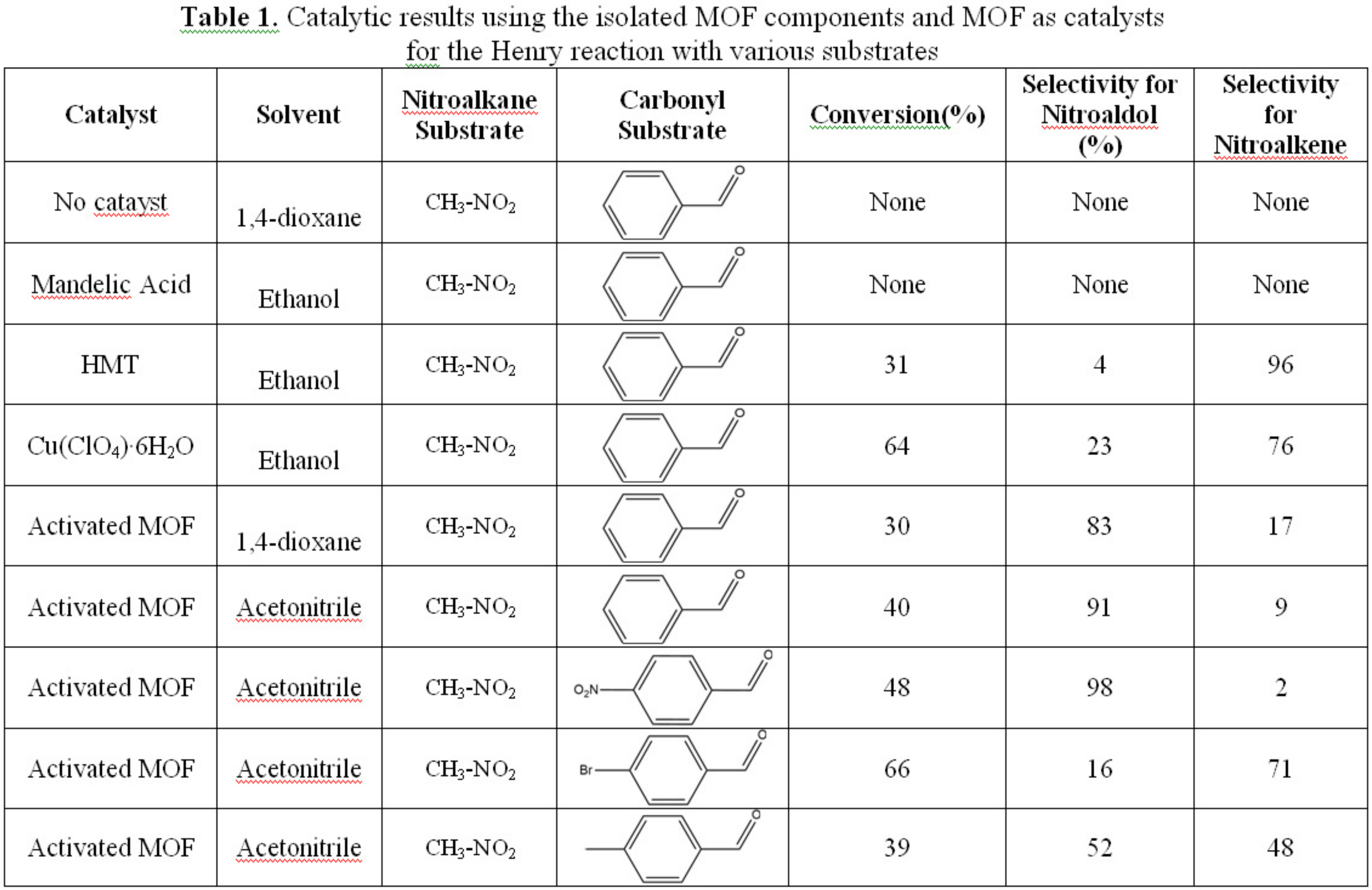
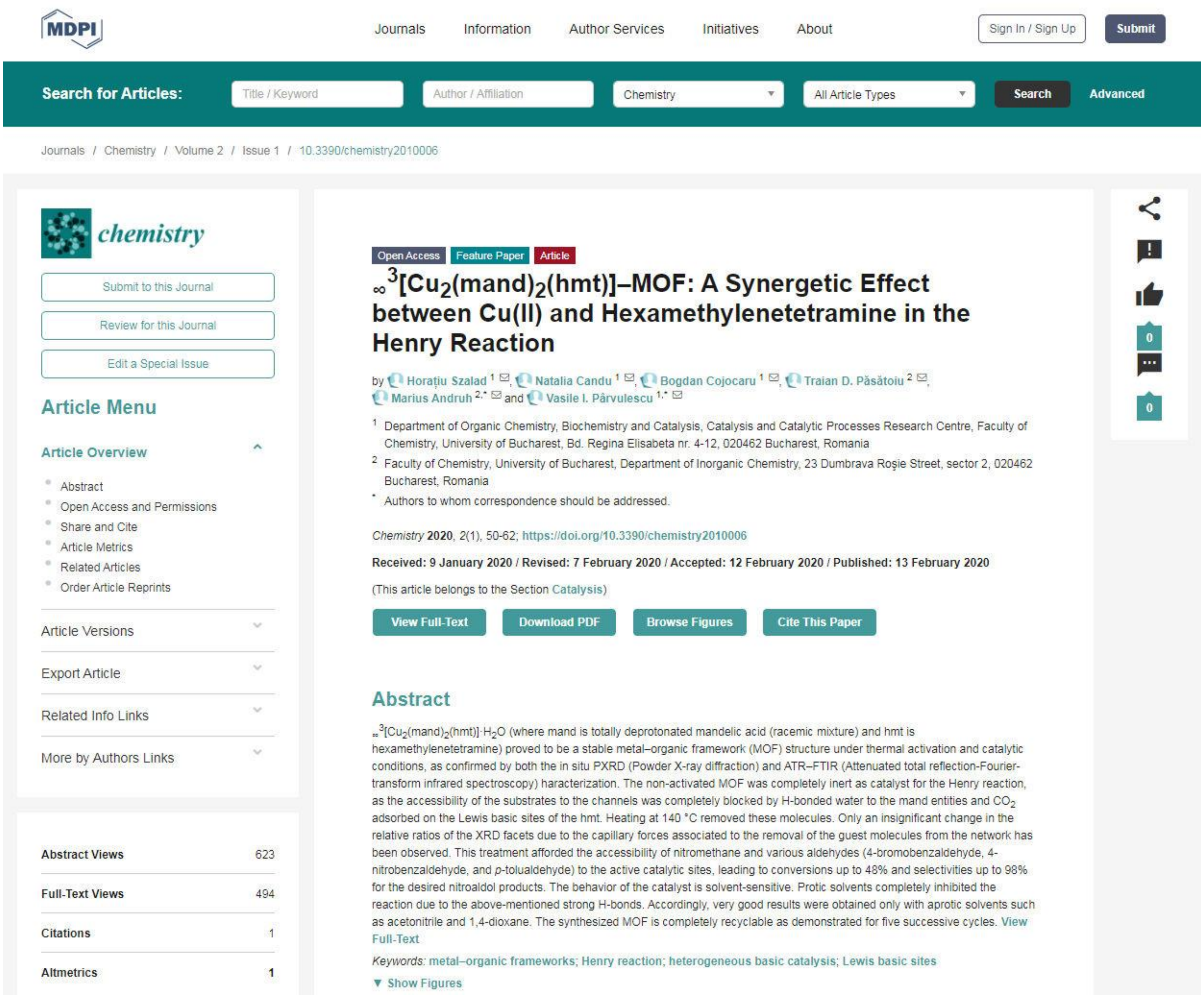


Table 1. Catalytic results using the isolated MOF components and MOF as catalysts for the Henry reaction with various substrates

Catalyst	Solvent	Nitroalkane Substrate	Carbonyl Substrate	Conversion(%)	Selectivity for Nitroaldol (%)	Selectivity for Nitroalkene
No catayst	1,4-dioxane	CH_3-NO_2		None	None	None
Mandelic Acid	Ethanol	CH_3-NO_2		None	None	None
HMT	Ethanol	CH_3-NO_2		31	4	96
$Cu(ClO_4)\cdot6H_2O$	Ethanol	CH_3-NO_2		64	23	76
Activated MOF	1,4-dioxane	CH_3-NO_2		30	83	17
Activated MOF	Acetonitrile	CH_3-NO_2		40	91	9
Activated MOF	Acetonitrile	CH_3-NO_2	O_2N	48	98	2
Activated MOF	Acetonitrile	CH_3-NO_2	Br	66	16	71
Activated MOF	Acetonitrile	CH_3-NO_2		39	52	48

Horatiu Szalad, **Natalia Candu, Traian Pasatoiu, Marius Andruh, Vasile Parvulescu** - *$_\infty[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction* (poster) - RomCat2019. The 12th International Symposium of the Romanian Catalysis Society, Bucureşti, România, 5-7th June 2019



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Altmetrics	**1**

${}_{\infty}^{3}[Cu_2(mand)_2(hmt)]$–MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction

by Horațiu Szalad [1], Natalia Candu [1], Bogdan Cojocaru [1], Traian D. Păsătoiu [2], Marius Andruh [2,*] and Vasile I. Pârvulescu [1,*]

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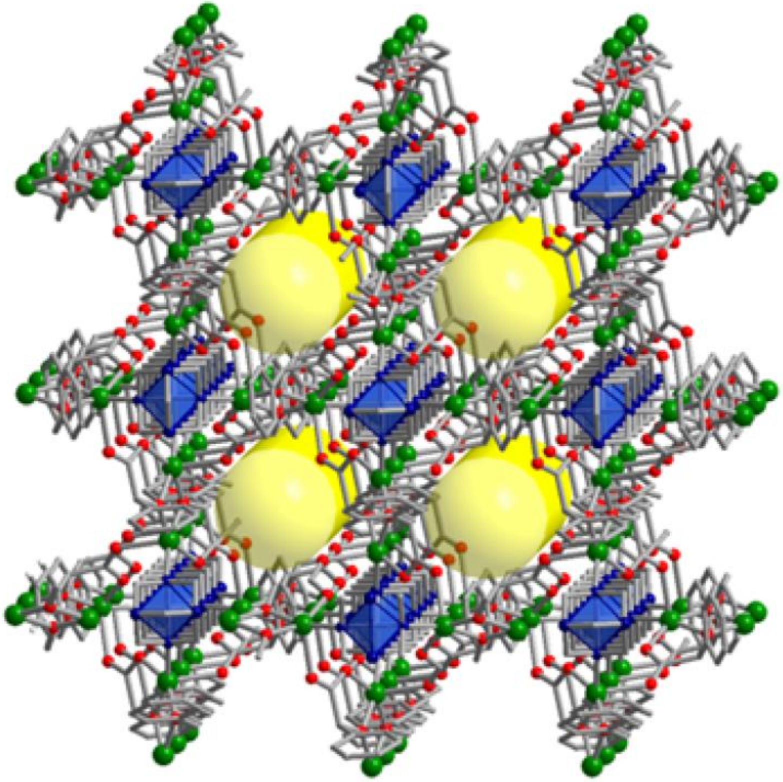
(This article belongs to the Section Catalysis)

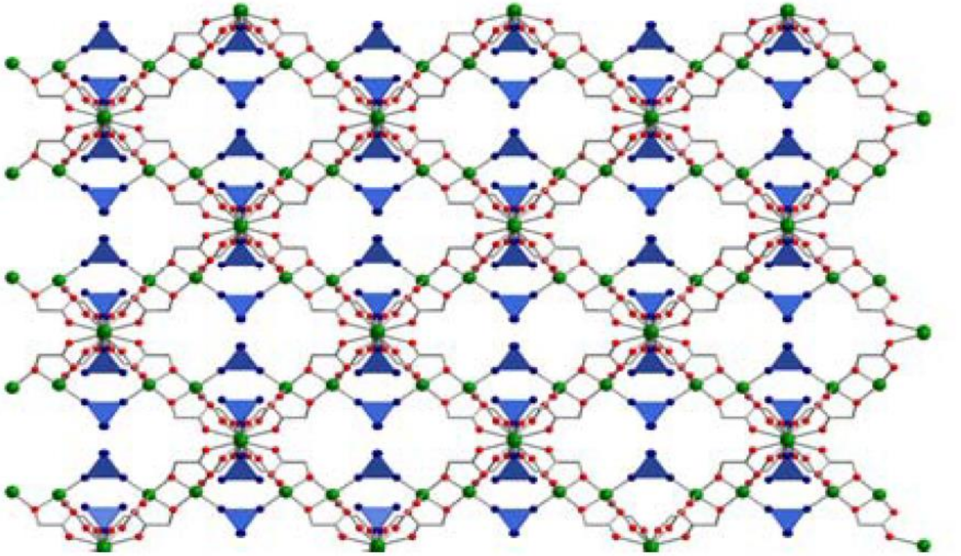
Abstract

${}_{\infty}^{3}[Cu_2(mand)_2(hmt)]\cdot H_2O$ (where mand is totally deprotonated mandelic acid (racemic mixture) and hmt is hexamethylenetetramine) proved to be a stable metal–organic framework (MOF) structure under thermal activation and catalytic conditions, as confirmed by both the in situ PXRD (Powder X-ray diffraction) and ATR–FTIR (Attenuated total reflection-Fourier-transform infrared spectroscopy) haracterization. The non-activated MOF was completely inert as catalyst for the Henry reaction, as the accessibility of the substrates to the channels was completely blocked by H-bonded water to the mand entities and CO_2 adsorbed on the Lewis basic sites of the hmt. Heating at 140 °C removed these molecules. Only an insignificant change in the relative ratios of the XRD facets due to the capillary forces associated to the removal of the guest molecules from the network has been observed. This treatment afforded the accessibility of nitromethane and various aldehydes (4-bromobenzaldehyde, 4-nitrobenzaldehyde, and *p*-tolualdehyde) to the active catalytic sites, leading to conversions up to 48% and selectivities up to 98% for the desired nitroaldol products. The behavior of the catalyst is solvent-sensitive. Protic solvents completely inhibited the reaction due to the above-mentioned strong H-bonds. Accordingly, very good results were obtained only with aprotic solvents such as acetonitrile and 1,4-dioxane. The synthesized MOF is completely recyclable as demonstrated for five successive cycles. View Full-Text

Keywords: metal–organic frameworks; Henry reaction; heterogeneous basic catalysis; Lewis basic sites

${}_{\infty}{}^{3}[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction

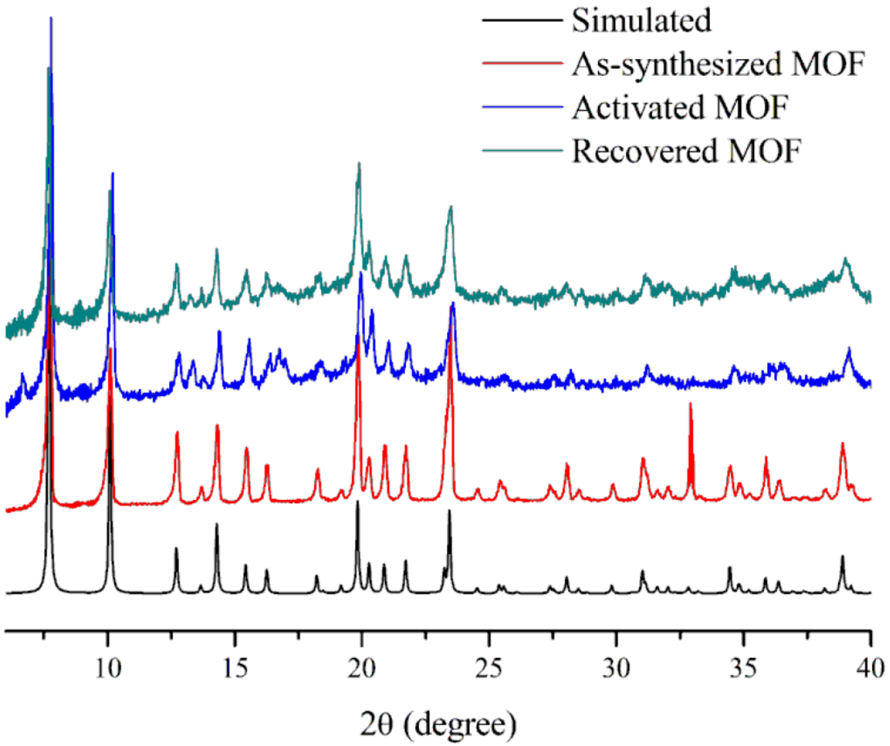




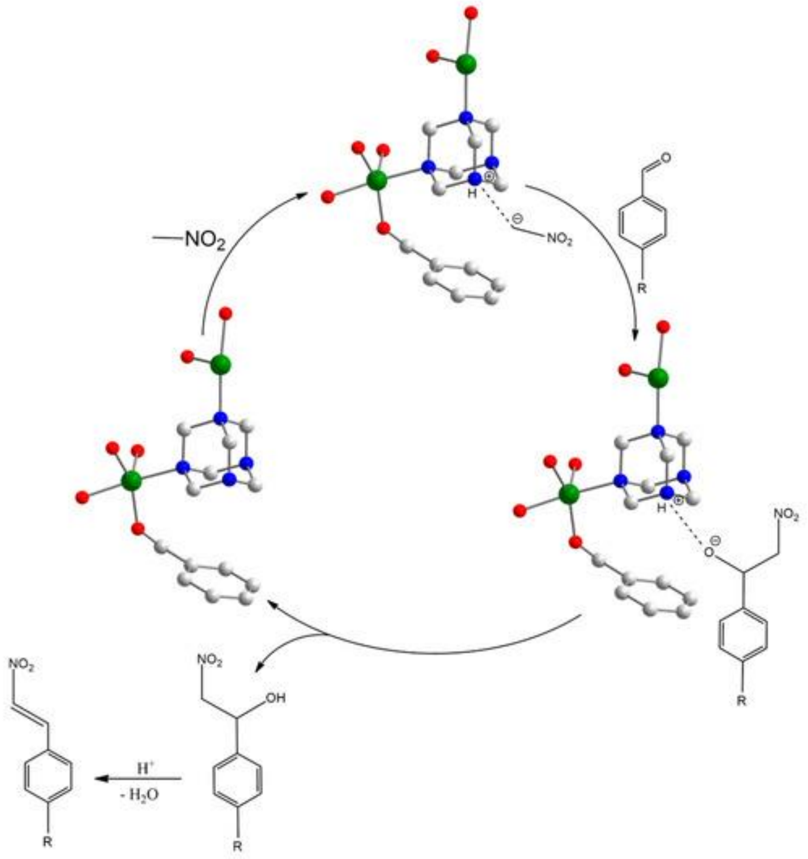
Perspective views of ${}_{\infty}{}^{3}[Cu_2(mand)_2(hmt)]$ - hmt molecules are drawn in blue; channels hosting the water molecules are drawn in yellow (left); view along the crystallographic *b* axis emphasizing the hmt molecules (blue) each one with two uncoordinated nitrogen atoms (right).

Horatiu Szalad, Natalia Candu, Bogdan Cojocaru, Traian Pasatoiu, Marius Andruh, Vasile Parvulescu *Chemistry* **2020**, *2*, 50-62
(https://doi.org/10.3390/chemistry2010006)

${}_{\infty}^{3}[Cu_2(mand)_2(hmt)]$ – MOF: A Synergetic Effect between Cu(II) and Hexamethylenetetramine in the Henry Reaction



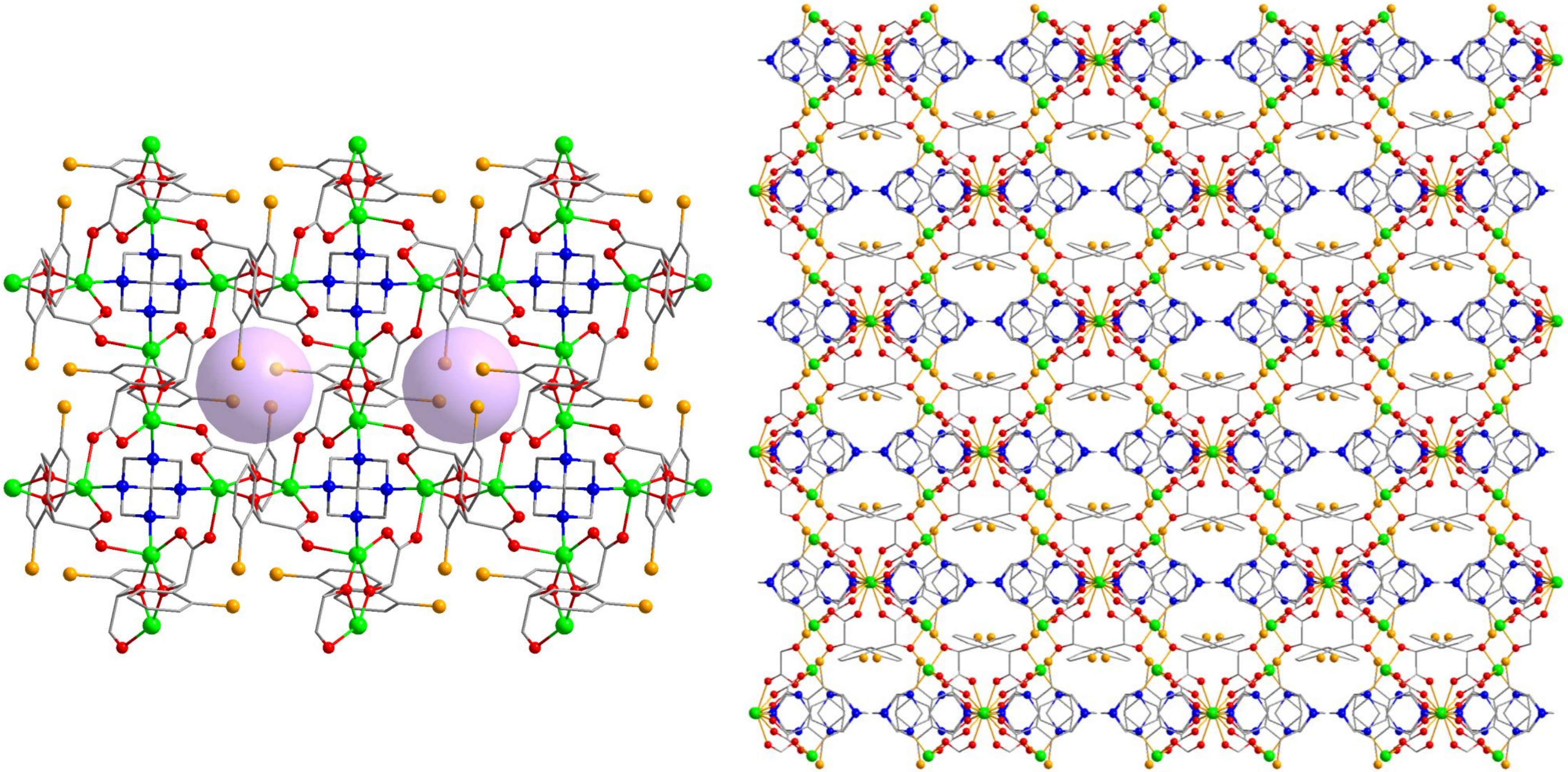
The XRD powder patterns for the simulated, as synthesized, activated, and recovered MOF



The catalytic cycle for the Henry reaction facilitated by the ${}_{\infty}[Cu_2(mand)_2(hmt)]$ MOF catalyst
(Cu - green, O - red, N - blue, C – gray; H atoms are omitted for clarity)

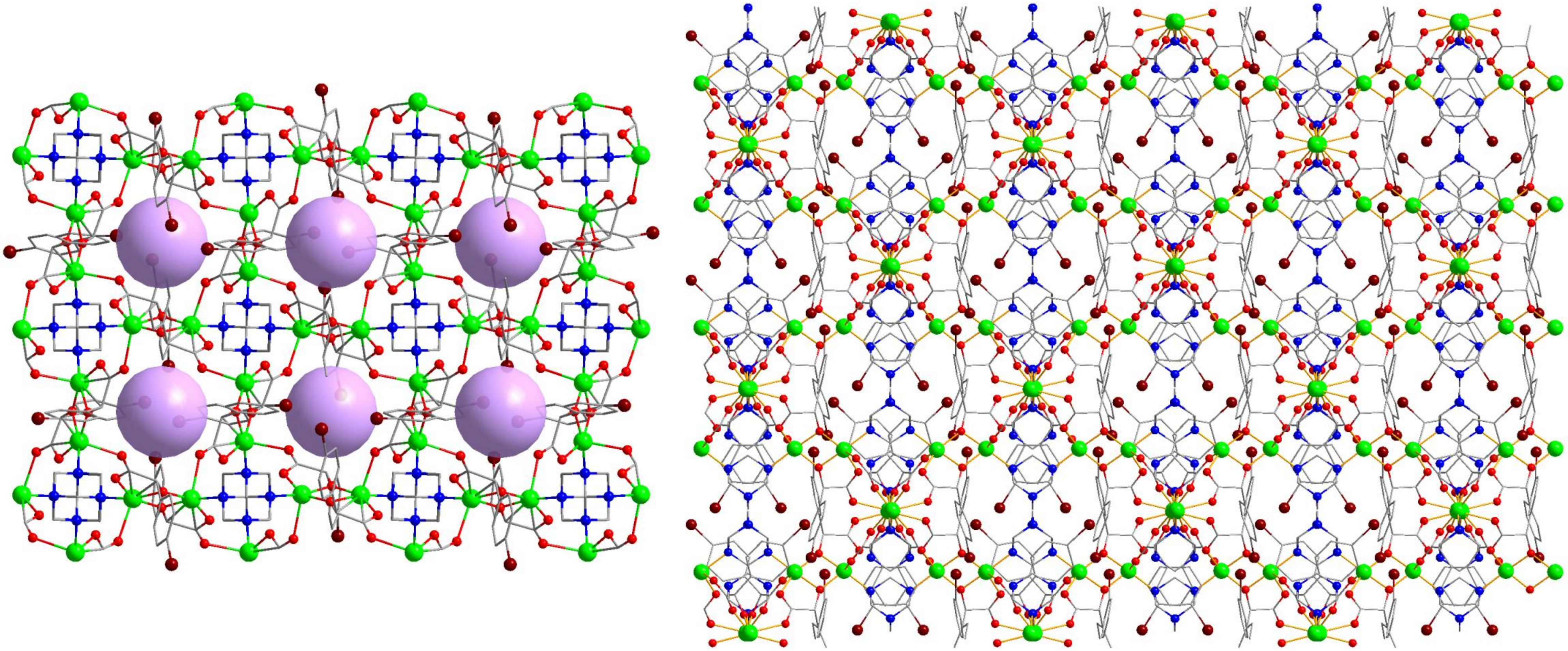
Horatiu Szalad, Natalia Candu, Bogdan Cojocaru, Traian Pasatoiu, Marius Andruh, Vasile Parvulescu *Chemistry* **2020**, *2*, 50-62
(https://doi.org/10.3390/chemistry2010006)

New Metal-Organic Frameworks - $_{\infty}^{3}[\mathrm{Cu_2(2\text{-}Cl\text{-}mand)_2(hmt)}]$



Perspective views of $_{\infty}^{3}[\mathrm{Cu_2(2\text{-}Cl\text{-}mand)_2(hmt)}]$: along the crystallographic *c* axis (left) and *a* axis (right).
hmt molecules are drawn in blue; channels are drawn in violet

New Metal-Organic Frameworks - ${}_{\infty}^{3}[\mathrm{Cu_2(4\text{-}Br\text{-}mand)_2(hmt)}]$



Perspective views of ${}_{\infty}^{3}[\mathrm{Cu_2(4\text{-}Br\text{-}mand)_2(hmt)}]$: along the crystallographic *c* axis (left) and *b* axis (right). hmt molecules are drawn in blue; channels are drawn in violet