Metallomacrocycles and Metal Organic Frameworks Based on Pyridine Carboxylate Ligands: Synthesis, Characterization and Applications

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Abstract: This work consisted on the preparation of various molecular complexes, metallomacrocycles and metal organic frameworks (MOFs) using novel carboxylate linkers in the presence of transition metals, and the study of their catalytic and sensing properties. Three new pro-ligands based on pyridine carboxylates namely, 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid (H_4L1), 3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)}dibenzoic acid (H_2L2) and 4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H_2L3) were synthesized and characterized by ^{1}H-NMR and FT-IR. Upon the reaction of the above mentioned pro-ligands with metal salts of Co(II), Cu(II), Zn(II), Cd(II) and Sm(III) ten novel compounds have been synthesized. They were characterized by FT-IR and single crystal X-ray diffraction analysis which revealed different nuclearities and topologies for the compounds. Their catalytic properties of the metal complexes were evaluated towards the Henry reaction, Knoevenagel condensation, microwave-assisted solvent-free peroxidative oxidation of a secondary alcohol and oxidation of toluene. Sensing properties have also been tested for some of the compounds and high sensitivity and selectivity towards Fe^{3+}, Fe^{2+} and MnO_4^- ions were achieved.

Keywords: MOF; crystalline structure; heterogeneous catalysis; chemical sensor; Henry reaction; Knoevenagel condensation.

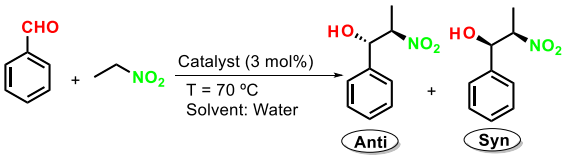
1. Introduction

Metal organic frameworks (MOFs) are a class of compounds which can be synthesized under mild conditions using multidentate organic linkers and metal ions or clusters, forming crystalline structures. Due to their high porosity and consequent high surface area, coupled with other properties, these compounds are guest responsive materials with a variety of abilities in catalysis, storage, sensing, and many others chemistry fields.[1-4] There are many synthetic pathways to synthesize MOFs including traditional synthesis, hydro or solvothermal, microwave, electrochemical, mechanochemical and sonochemical, among others.

The application of MOFs as heterogeneous catalysts has proved to be highly advantageous,[5] in view of their well-defined pores and channels which enables them to be size- and shape-selective catalysts. Active coordinately unsaturated metal sites can be introduced into MOFs either as metal connecting points or as part of the linker.

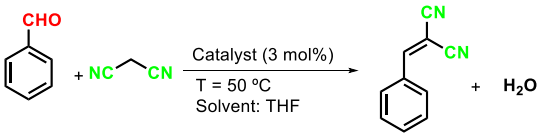
The application of these compounds as heterogeneous catalysts includes several organic transformations, such as:

i) the Henry (nitroaldol) reaction, which is the combination of a nitroalkane and an aldehyde or ketone, in the presence of a base, to form β-nitro alcohols that can have, depending on the nitroalkane, two isomeric forms the *syn* and the *anti* (Scheme 1).[6]



Scheme 1 - Nitro-aldol (Henry) reaction between benzaldehyde and nitroethane.

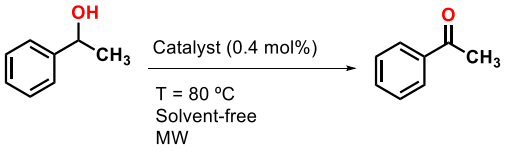
ii) the Knoevenagel condensation (Scheme 2), where a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction, allows the formation of a nitroalkene, which is a kind of valuable synthetic intermediate. Limited examples have been reported on the use of metal organic frameworks as catalysts in the Knoevenagel condensation, but those cases have already shown great possibilities of these compounds.[7]



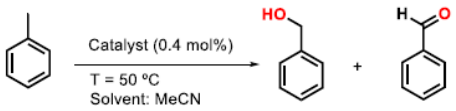
Scheme 2 - Knoevenagel condensation reaction between benzaldehyde and malononitrile.

iii) microwave-assisted solvent-free peroxidative oxidation of secondary alcohols to the corresponding ketone (Scheme 3).

iv) the oxidation of toluene to benzyl alcohol and benzaldehyde, a kind of transformation also interesting to the pharmaceutical industry (Scheme 4).



Scheme 3 - Oxidation of 1-phenylethanol to acetophenone, by a microwave-assisted solvent-free reaction.



Scheme 4 - Oxidation reaction of toluene into benzyl alcohol and benzaldehyde.

The use of MOFs in microwave-assisted solvent-free peroxidative oxidation of 1- phenylethanol and the oxidation of toluene under mild conditions have already been reported.[8,9]

MOFs are also relevant in chemical sensing. Chemical sensors are complex devices that must be optimized for an application, and they typically must be operated at high temperatures (above 200 ºC) to promote a reaction.[10] In this respect, MOFs are thermally robust.[11,12] Poisoning of the sensor is another common limitation. For example, H_2 sensors based on reversible, dissociative uptake of H_2 by films of elemental palladium are susceptible to poisoning by CO and H_2S. [13]

One way to detect very low concentrations of an analyte is by luminescence quenching.[14] In the case of luminescent metal organic frameworks (LMOFs), the best way is to incorporate luminescent metal centers, where common choices are lanthanide ions. In the solid state, electronic interactions (such as ligand to ligand charge transfer) can affect luminescence.[15] The detection technique may be based on the fluorescence emission wavelength shifts which depend on the presence and identity of the guest species in the LMOF,[16] or on intensity changes, where enhancement or quenching of luminescence may occur.[17] In some cases, it has been reported that LMOF can recognize and sense both anions and cations.[18,19]

The construction of metal organic frameworks depends entirely on the type of ligands used. Polycarboxylic acids are among the most attractive building blocks leading to stable MOFs with permanent porosity. [20-22]

In this work, the choice of pyridine based amide carboxylic acid pro-ligands, was due to the following characteristics: (a) the carboxylate groups can be partially or completely deprotonated by tuning the reaction pH and thus the formation of multidimensional MOFs could be expected; (b) the flexible amide arm of pro-ligands can adopt various conformations, which would further generate diverse architectures; (c) the introduction of an amide functionality can offer additional hydrogen bonding sites as well as a Lewis-basic nature to the frameworks. Pro-ligands 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid (H_4L1), 3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H_2L2) and 4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H_2L3) have been synthesized and characterized (Figure 1). The reaction of the above mentioned pro-ligands with different metal salts of Co(II), Zn(II), Cu(II), Cd(II) and Sm(III), produced the following new compounds: $[Co(H_2L1)(MeOH)_4].MeOH$ (**1**), $[Zn_2(L1)(H_2O)_4]_n.4n(H_2O)$ (**2**), $[Cd_3(HL1)_2(DMF)_4]_n.2n(DMF)$ (**3**), $[Cu_4(L2)_2(NO_3)_2(OH)_2(MeOH)_2].MeOH$ (**4**), $[Cu_2(L2)(DMF)_2]_n$ (**5**), $[Zn(L2)(H_2O)_2]_n$ (**6**), $[Cd_2(L2)_2(H_2O)_4]_n.3nH_2O$ (**7**), $[Sm_3(L2)(DMF)(NO_3)(H_2O)_4]_n.nDMF$ (**8**), $[Zn_2(L3)_2(H_2O)_4].2H_2O.3DMF$ (**9**) and $[Zn_5(L3)_4(OH)_2(H_2O)_4]_n$ (**10**).

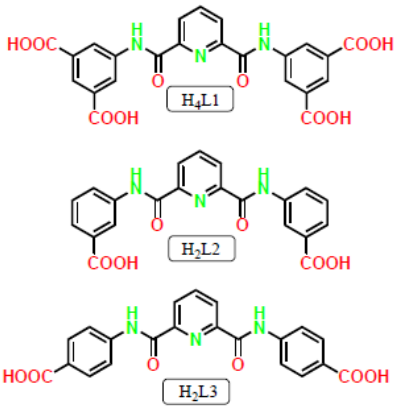


Figure 1 - The pro-ligands used in the MOFs construction

2. Experimental Section

The synthetic work was performed in air. All the chemicals were obtained from commercial sources and used as received.

The ^{1}H-NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShieldMagnet) spectrometer operating at 300 MHz for proton. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. ^{1}H abbreviations: s = singlet, d = doublet, t = triplet, q = quartet.

The infrared spectra (FT-IR, 4000-400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets. Abbreviations: s = strong, m = medium, w = weak, bs = broad and strong, mb = medium and broad.

The microwave-assisted (MW) solvent-free peroxidative oxidation of 1-phenylethanol was carried out in a focused Anton Paar Monowave 300 reactor using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector.

X-ray quality single crystals of compounds **1**-**10** were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature. Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromatic Mo-Kα (λ=0.71069) radiation.

The products of the catalyzed oxidation reactions were analyzed by gas chromatography, by using

a Fisons Trio 2000 Gas Chromatography/Mass Spectrometer.
The fluorescence spectra were recorded on a Spectrofluorimeter Perkin Elmer LS55 Perkin Elmer Lambda 35, using quartz cells.

2.1 Synthesis of the compounds

The synthesis of 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid (H_4L1) was achieved by the condensation of the methyl ester of 5-aminoisophthalic acid with 2,6-pyridinedicarboxylic acid chloride in the presence of NEt_3, and hydrolyzed by NaOH/THF.
The synthesis of 3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H_2L2) and 4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H_2L3) are similar; 3–amino benzoic acid (for H_2L2) or 4-amino benzoic acid (for H_2L3), were esterified in the presence of methanol and sulfuric acid, followed by reactions with 2,6-pyridinedicarboxylic acid chloride in the presence of NEt_3, and the products hydrolyzed in the presence of NaOH and THF. Details of the reactions are described below.

Synthesis of H_4L1

The methyl ester of 5-aminoisophthalic acid (388 mg, 1.85 mmol) was dissolved in 20 mL of dichloromethane (DCM), followed by addition of a 5 mL DCM solution of 2,6-pyridinedicarboxylic acid chloride (204 mg, 1 mmol). 600 µL of trimethylamine was then added dropwise, the mixture was stirred overnight at room temperature and then taken to dryness. Upon addition of water and filtration to remove soluble unreacted reagents, the ester was dissolved in 30 mL of tetrahydrofuran followed by drop wise addition of an aqueous solution of NaOH (0.15 mol.dm^{-3}), refluxed for 1 hour and then stirred at RT overnight. The final mixture was taken to dryness. Addition of HCl led to the formation of a solid which was separated by filtration, washed with cold water and dried in air.

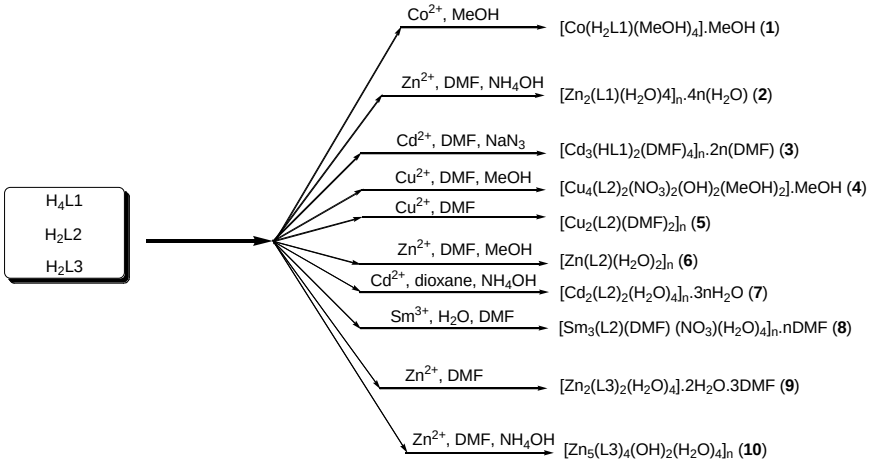
^{1}H-NMR (DMSO-d_6): 12.89 (2H, bs, -COOH), 11.21 (2H, s, -NH), 8.74 (2H, s, Ar-H), 8.67 (4H, s, Ar-H), 8.20-8.31 (3H, m, Ar-H). FT-IR (KBr, selected peaks) [cm^{-1}]: 3466 (bs), 1713 (s), 1649 (m), 1550 (s), 1453 (s), 1385 (w), 1296 (s), 1227 (m), 1147 (m), 1083 (m), 1000 (m), 908 (w), 844 (w), 758 (s), 667 (s), 601 (m).

Synthesis of H_2L2:

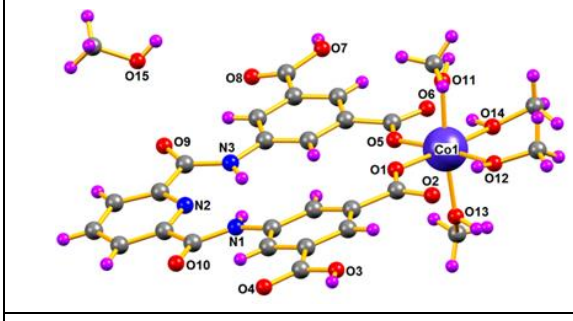
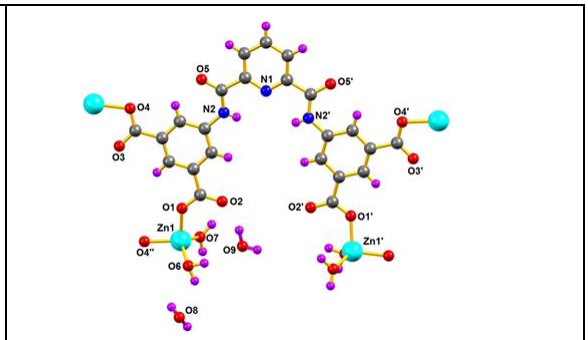
2g (0.015 mol) of 3-amino benzoic acid were dissolved in 20 mL MeOH, then concentrated sulfuric acid (8 mL) was added drop wise and the mixture refluxed overnight. After evaporation of the excess of unreacted MeOH, solid sodium bicarbonate ($NaHCO_3$) was added until neutralization. The mixture was then extracted with DCM (total of *ca.* 40 mL) and the organic solution dried with 1 – 2 g of sodium sulfate. The clear solution was then taken to dryness. The procedure for the synthesis of the final compound was then like that already described for H_4L1, using methyl ester of 3-amino benzoic acid instead of methyl ester of 5-aminoisophthalic acid.
^{1}H-NMR (DMSO-d_6): 13.18 (2H, bs, -COOH), 11.19 (2H, s, -NH), 8.56 (2H, s, Ar-H), 8.45 (2H, d, Ar-H), 8.18-8.35 (3H, m, Ar-H), 7.79 (2H, d, Ar-H), 7.60 (2H, t, Ar-H). FT-IR (KBr, selected peaks) [cm^{-1}]: 3462 (bs), 1701 (s), 1661 (s), 1591 (s), 1553 (m), 1487 (w), 1441 (s), 1297 (s), 1230 (m), 1141 (m), 1082 (m), 946 (m), 815 (m), 758 (s), 739 (s), 679 (s), 564 (w).

Synthesis of H_2L3:

We have synthesized H_2L3 using a similar procedure as mentioned above for H_2L2.
^{1}H-NMR (DMSO-d_6): 13.14 (2H, bs, -COOH), 11.27 (2H, s, -NH), 8.43 (2H, d, Ar-H), 8.34 (^{1}H, d, Ar-H), 8.05 (8H, m, Ar-H). FT-IR (KBr, selected peaks) [cm^{-1}]: 3447 (bs), 1689 (s), 1609 (s), 1537 (s), 1410 (s), 1320 (s), 1300 (s), 1242 (s), 1179 (s), 1120 (m), 1085 (m), 1000 (m), 932 (m), 854 (s), 770 (s), 748 (s), 714 (m), 552 (m).



*Scheme 5 - Synthesis of compounds **1**-**10**.*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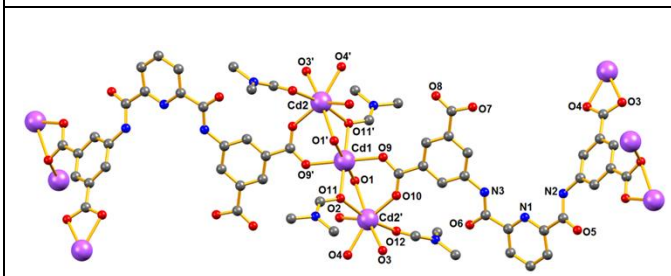
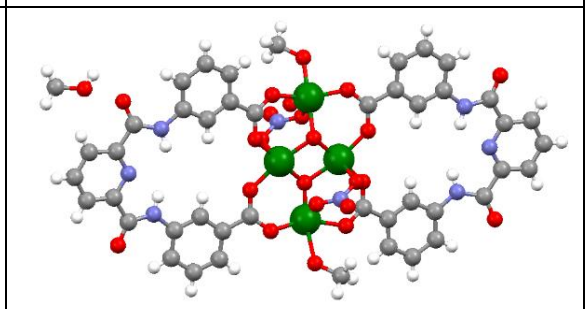
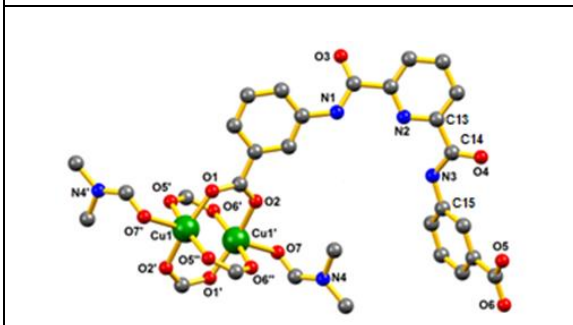
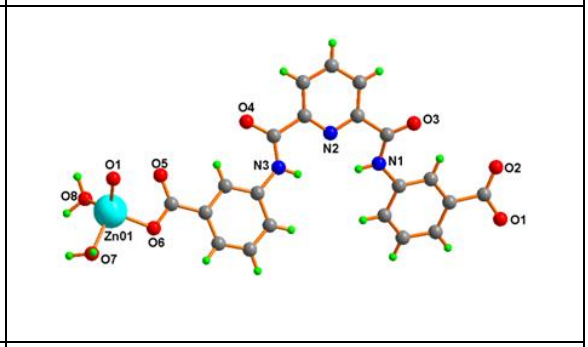
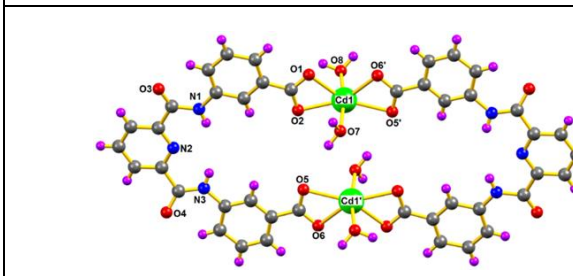
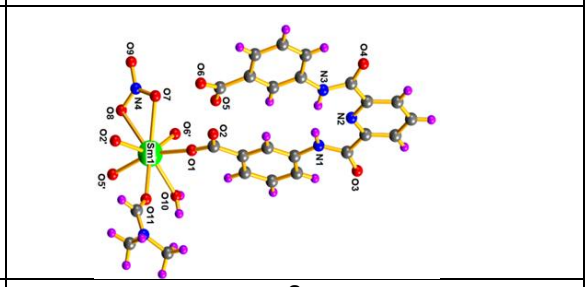
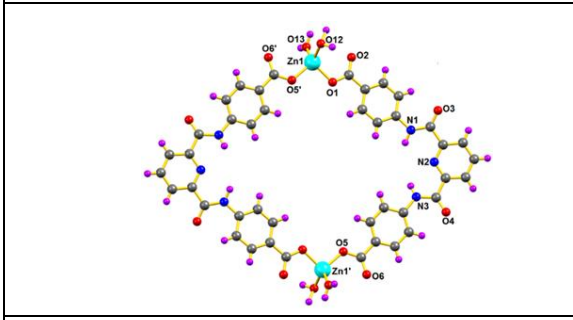
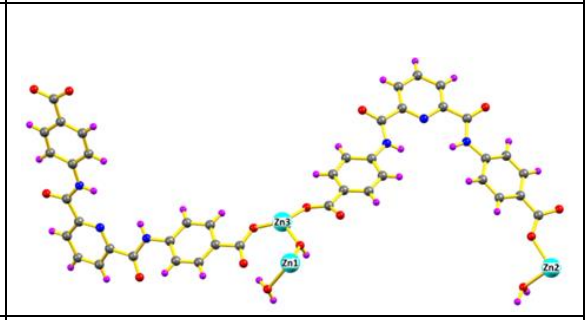
	
3	**4**
	
5	**6**
	
7	**8**
	
9	**10**

*Figure 2 - Crystalline structure of compounds **1**-**10**.*

Synthesis of the MOFs

The pro-ligands (0.025 mmol) were dissolved in 2 mL of an adequate solvent, or mixture of solvents (Scheme 5), and then 0.050 mmol of $Co(NO_3)_2{\cdot}6H_2O$ (for **1**), $Cu(NO_3)_2{\cdot}2.5H_2O$ (for **4** and **5**), $Zn(NO_3)_2{\cdot}6H_2O$ (for **2**, **6**, **9** and **10**), $Cd(NO_3)_2{\cdot}4H_2O$ (for **3** and **7**) or $Sm(NO_3)3{\cdot}6H_2O$ (for **8**) was added and the mixture sonicated until dissolution. This solution was then transferred to an 8 mL glass vessel, sealed and heated at 70ºC for 48h. After slow cooling to room temperature, crystals of compounds **1** - **10** were obtained, isolated by filtration and dried in air (see Figure 2).

2.2 Catalytic procedures

Henry (nitroaldol) reaction

To a 5 mL glass vessel, a mixture of benzaldehyde (52 µL, 0.5 mmol), nitroethane (0.2 mL, 2.6 mmol), water (1.0 mL) and 3.0 mol% of MOF catalyst was added, placed in an oil bath at a designated temperature (in typical conditions, 70 ºC) and the system was left under stirring for 48h. After addition of 1 mL of DCM and stirring, 1 mL of the organic phase was centrifuged (to separate the MOF) and the clean solution taken to dryness. After addition of 500 µL of $CDCl_3$ the sample was analyzed by ^{1}H-NMR.

Knoevenagel condensation

To a 5 mL glass vessel, a mixture of benzaldehyde (52 µL, 0.5 mmol), malononitrile (66 mg, 1 mmol), THF (1.0 mL) and 3.0 mol % of catalyst was added and then placed in an oil bath at a designated temperature (in typical conditions, 50 ºC). The system was left under stirring for 1.5h after which 1 mL of sample solution was centrifuged. After evaporation of the THF 500 µL of $CDCl_3$ was added, and the sample was analyzed by ^{1}H-NMR.

Microwave assisted solvent-free peroxidative oxidation of Benzaldehyde

In a Pyrex tube a mixture of 10 µmol of catalyst (generally 0.4 mol% of the substrate), 5 mmol of alcohol (1-phenylethanol) and t-BuOOH (10 mmol, 70%) were added and the cylindrical Pyrex tube was sealed and placed in the microwave under 10-25 W irradiation, at 80 or 120 °C for 1h. After addition of 300 µL of benzaldehyde (internal standard) and 5 mL of MeCN (to extract the substrate and the organic products from the reaction mixture) the obtained mixture was stirred for 10 min and then a sample (1 µL) from the organic phase was analyzed by GC. Blank experiments (absence of any MOF catalyst) were performed following the indicated conditions.

Oxidation of toluene

Toluene (0.610 mL, 5.7 mmol), 0.4% mol of catalyst (respectively 6.8 mg of **4** and 10.8 mg of **5**), acetonitrile (3 mL) and hydrogen peroxide H_2O_2 (1.02 mL; 33.3 mmol) were mixed in a 6 mL glass vessel, sealed and left under stirring at 50 °C for 24h, after which 90 µL of cycloheptanone (internal standard) and 10 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. This mixture was stirred for 10min and then a sample (1 µL) of the organic phase was analyzed by GC. Blank experiments (absence of any MOF catalyst) were performed following the indicated conditions.

2.3 Sensing studies

3 mg of MOF were dispersed in 3 mL of 10^{-2} mol.dm^{-3} solutions of MCl_z [M = Li(I), Na(I), Ca(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Nb(V), z=1,2 or 5] or M_zX [M = Na, X = NO_3^-, HCO_3^-, OAc^-, NO_2^-, Cl^-, HPO_4^{2-}, N_3^-, CO_3^{2-}, BF_4^-, SO_4^{2-}, SCN^- ; M = K, X = MnO_4^-, F-, CO_3^{2-}, Cl^-, Br^-, z=1 or 2] in a 10 mL glass tube and stirred for 1h, left resting for 48h, after which their fluorescence intensities were measured.

Results and Discussion

In the FT-IR spectra of H_4L1, H_2L2 and H_2L3, the characteristic strong bands of the amine groups appear between 3447 and 3466 cm^{-1}. C–O stretching of carboxylate group is observed between 1296 and 1300 cm^{-1}. C=O stretching is observed between 1689 and 1713 cm^{-1}. In the ^{1}H-NMR spectra, the resonance of the carboxylic hydrogens appears amid 12.89-13.18 ppm and that of the amide hydrogen at 11.19-11.27 ppm.

- **Characterization of compounds 1-10**

Compound **1** features a mononuclear Co(II) complex, compound **2** is a layer type two-dimensional framework and compound **3** is a two-dimensional framework. In FT-IR, the C-O bands appear between 1227 cm^{-1} and 1298 cm^{-1}, which agrees with data collected from H_4L1 ligand (1296 cm^{-1}).
Compound **4** features a tetranuclear complex, compound **5** is a two-dimensional framework, compound **6** features a zig-zag type one dimensional polymeric chain, compound **7** is a dimeric metallomacrocyclic complex and compound **8** presents a 1D network. In FT-IR, the C-O stretching appear between 1160 cm^{-1} and 1385 cm^{-1}, which agrees with data collected from H_2L2 ligand (1297 cm^{-1}).
Compound **9** is a dimeric metallomacrocycle, and compound **10** reveals that it is a two-dimensional infinite framework. In FT-IR, the C-O bands appear between 1180 cm^{-1} and 1281 cm^{-1}, which agrees with data collected from H_2L3 ligand (1300 cm^{-1}) (Scheme 5 and Figure 2).

- **Catalytic studies**

Catalytic Activity of MOFs in the Henry (nitroaldol) reaction:

The activity of the coordination polymers **1**-**3** and **6**-**10** were tested towards the Henry (nitroaldol) reaction of benzaldehyde with nitroethane.
Compound **3** led to the highest product yield, as compared to the other compounds, after the same

reaction time and temperature (see Figure 3). The optimization of the reaction conditions (temperature, reaction time, amount of catalyst, solvent) was carried out in a model with **3** as the catalyst (see Figure 4).

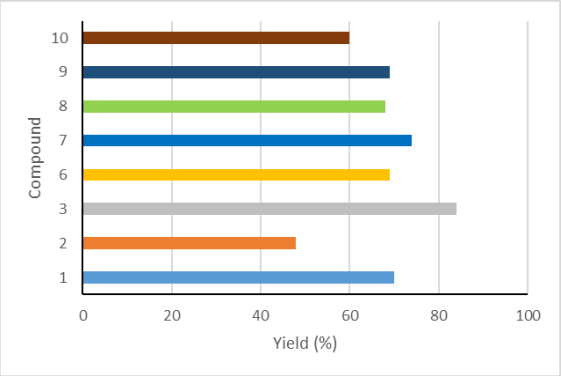


Figure 3 - Reaction yields using different catalysts at the optimized reaction conditions.

Under the optimal conditions (3 mol% of solid **3**, 70 ºC with water) a conversion of 84% of benzaldehyde into the β-nitroalkanol is reached after 48 h.
Blank reaction was tested with benzaldehyde in the absence of catalyst and no conversion of aldehyde in to product was detected.

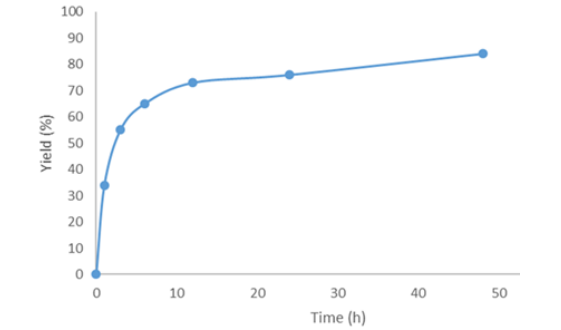


*Figure 4 - Reaction yield dependence on time, using catalyst **3** in optimal conditions.*

The activity of compound **3** in the reactions of a variety of para-substituted aromatic aldehydes, cinnamaldehyde and acetaldehyde with nitroethane was also tested, and obtained the corresponding β-nitroalkanols with yields ranging from 21 to 99 % aryl aldehydes bearing electron-withdrawing groups (nitro, chloro and hydroxy) exhibit higher reactivity as compared to those having electron-donating moieties (see Figure 5). Proposed catalytic cycle for the Henry reaction catalyzed by compound **3** is in Figure 6.

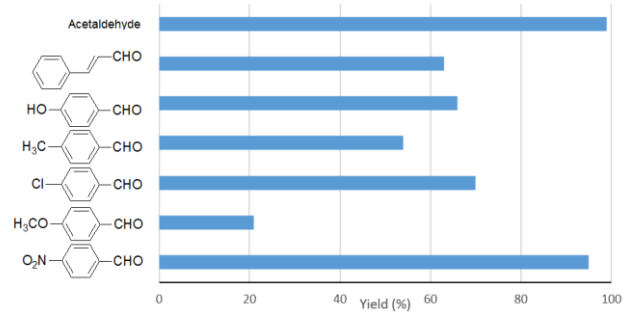


*Figure 5 - Henry reaction catalyzed by compound **3** using different para-substituted aldehydes, acetaldehyde and cinnamaldehyde, at optimal reaction conditions.*

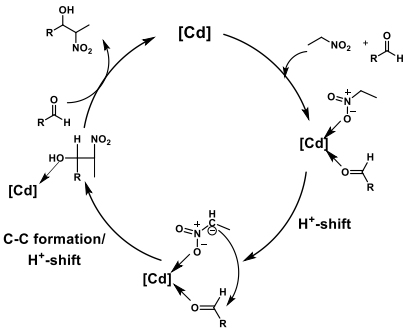


*Figure 6 - Proposed catalytic cycle for compound **3** in the Henry reaction.*

Catalytic Activity of MOFs in the Knoevenagel condensation

We have also tested the activity of the coordination polymers **1** – **3** and **6** – **10** as heterogeneous catalysts in the Knoevenagel condensation reaction. By using benzaldehyde as a test compound, we found that **9** led to the highest product yield, as compared to the other polymers after the same reaction time and temperature (Figure 7). The optimization of the reaction conditions (temperature, reaction time, amount of catalyst, solvent) was carried out in a model malononitrile – benzaldehyde system with **9** as the catalyst (Figure 8).

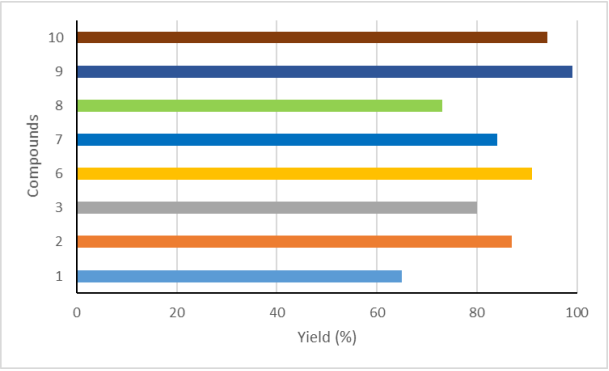


Figure 7 - Reaction yields using different catalysts at the optimized reaction conditions.

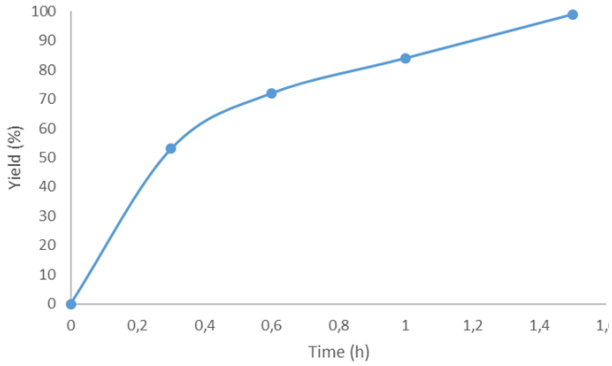


*Figure 8 - Reaction yield dependence on time, using catalyst **9** in optimal conditions.*

The Knoevenagel condensation reaction of various aldehydes with malononitrile catalyzed by compound **9** was also tested, producing the corresponding αβ-unsaturated ketone with yields ranging from 32 to 100 % (Figure 9).
The aldehydes containing electron-withdrawing groups exhibit higher reactivity as compared to those having electron-donating moieties, which may be related to an increase of the electrophilicity of the substrate in the former case.
In figure 10 in is presented the proposed catalytic cycle for the Knoevenagel reaction catalyzed by compound **9**.

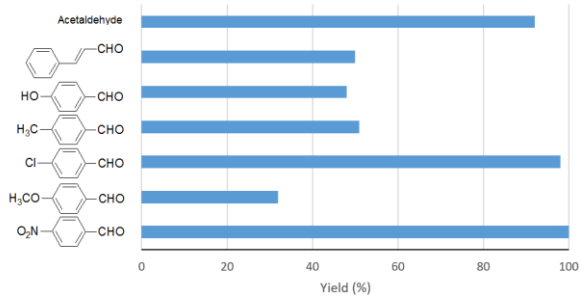


*Figure 9 - Knoevenagel condensation reaction catalyzed by compound **9** using different para-substituted aldehydes, acetaldehyde and cinnamaldehyde, at optimal reaction conditions.*

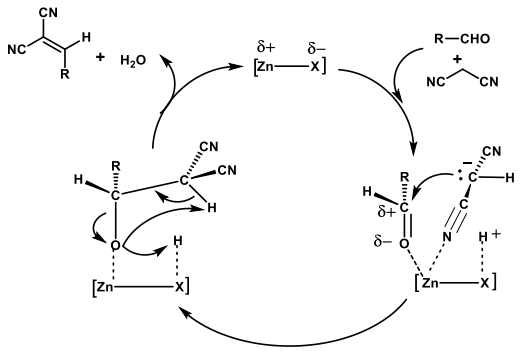


*Figure 10 - Proposed catalytic cycle for compound **9** in the Knoevenagel condensation reaction.*

Microwave-assisted solvent-free peroxidative oxidation of 1-Phenylethanol

We have also tested the catalytic activity of the coordination polymers **4** and **5** as heterogeneous catalysts in microwave-assisted peroxidative oxidation carried out under mild conditions, using *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant (Figure 11).
Under typical reaction conditions (80 ºC, 1h reaction time and 20 µmol of catalyst) yields of acetophenone were obtained up to 8% (TON = 75) for catalyst **4** and 11% (TON = 95) for catalyst **5**, in the absence of any additive. Acetophenone is the only product detected in the assayed conditions.
With the aim to increase the yields of the reaction in solvent-free MW-assisted peroxidative oxidation of the above-mentioned substrate, the influence of 2,2,6,6-tetramethylpiperidyl-1-oxyl radical (TEMPO) was investigated.[23]
However, contrary to what was previously observed, we found that the addition of TEMPO has an inhibition effect on the yield of reaction. We also found that increasing the amount of catalyst does not increase the yield of reaction.
The temperature has an important effect on the catalytic system, since changing the temperature from 80 ºC to 120 ºC results in a yield increase from 8% to 43% for compound **4** and 11% to 42%, in the case of **5**. Further conditions will be investigated in the future, to analyze the influence of the additives in the deactivation of the catalyst, and what would be the ideal reaction temperature.

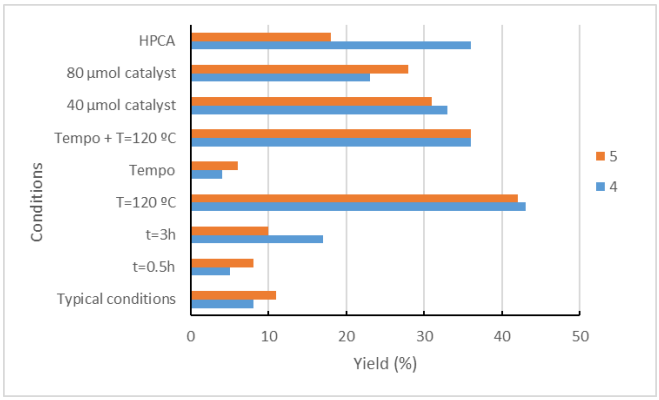


*Figure 11 - Reaction yields in peroxidative oxidation of 1-phenylethanol at different condition, using compounds **4** and **5**.*

Oxidation of toluene

We have also tested the catalytic activity of the coordination polymers **4** and **5** as heterogeneous catalysts in the peroxidative oxidation of toluene, using hydrogen peroxide (H_2O_2) as oxidant (Figure 12).
Under optimized reaction conditions benzaldehyde yields are very modest (maximum of 5% yield for catalyst **4** and 6% for catalyst **5**). With the aim to increase the activity of **4** and **5** in the oxidation of toluene the influence of additives was investigated. In the case of catalyst **4**, there is an increase of 2% with the addition of HNO_3 or TFA and in the case of

catalyst **5**, the use of additives had an opposite effect (a decrease of 2% in the yield).
Further conditions will be investigated in the future, to analyze the influence of additives and of temperatures in the reaction yields and, furthermore, why in the case of oxidation of toluene, the catalytic activity is so low.

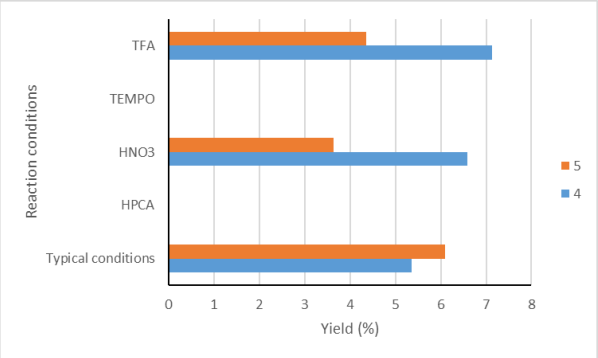


*Figure 12 - Reaction yields in the oxidation of toluene under different conditions, using compounds **4** and **5**.*

– **Sensing studies**

We also investigated the sensing properties of compound **2**. In compound **2**, the emission peak appeared at 438 nm upon excitation at 310 nm (Figure 13). Also, as the previous case, this emission band can be assigned to ligand-centered emission. As a preliminary analysis, we found that the luminescence spectra of compound **2** dispersed in the ionic aqueous solutions, was quenched by Fe(II), Fe(III) and MnO_4^- ions. More studies need to be done, but these preliminary results demonstrate that **2** can be effective and selective luminescent sensor for Fe(II), Fe(III) and MnO_4^- ions.

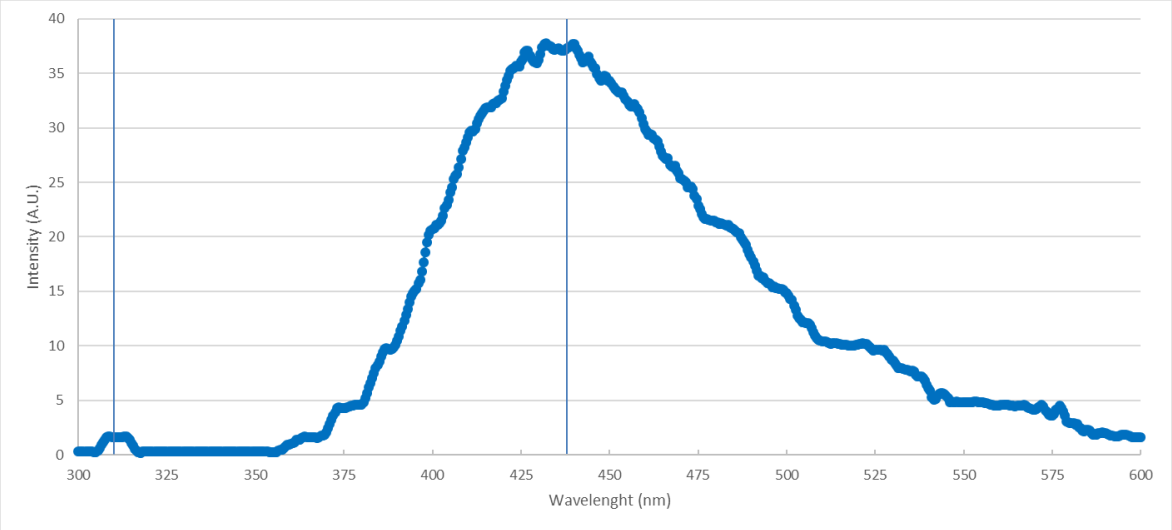


*Figure 13 – Blank spectra (solvent + compound **2**) showing excitation and emission bands at 310nm and 438nm for the fluorescence of compound **2**.*

Conclusions

In a first analysis, the choice of the pro-ligands for the architectural structure of metal organic frameworks considers some generic ideas on possible interactions between amide and carboxylic groups with the metal ions. In that sense, three new pro-ligands based on pyridine carboxylates have been synthesized and characterized: H_4L1, H_2L2 and H_2L3. Although it is guessable the possible locations for N-H…..Metal or O-H…..Metal coordination sites, metal organic frameworks have shown some amazing possibilities. The interactions not only in some specific sites, but with all the structure, allows to construct some amazing architectures. It allowed the discovery of 10 new compounds, with very interesting properties in the field of catalysis and sensing. Compound **1** and **4** features a mononuclear and a tetranuclear complex, respectively. Compound **7** and **9** features a metallomacrocycle type structure. The remaining compounds are 1-dimensional (**8** and **6**) or 2-dimensional (**2**, **3**, **5** and **10**) metal organic frameworks. The catalytic properties of all the compounds have been studied, and we found out that compound **3** act as effective heterogeneous catalyst for the Henry (nitroaldol) reaction (Yield=84%, in 48h at T=70 ºC), whereas compound **9** act as effective heterogeneous catalyst for the Knoevenagel condensation reaction (Yield=99%, in 1.5h at T=50 ºC) and compound **4** act as a modest heterogeneous catalyst, for microwave-assisted solvent-free peroxidative oxidation of 1-phenyl ethanol (Yield=43%, in 1h at T=120 ºC). Sensing properties of **2** have also been tested. This compound has sensitivity and selectivity for Fe^{3+}, Fe^{2+} and MnO_4^- ions and the fluorescence of compound **2** is completely quenched by these three

ions, which suggests that the synthesized MOFs are promising luminescent probes for selectively sensing iron and permanganate ions. We see conditions to analyze in more detail the sensing properties of these compounds, with in depth sensing studies, in the detection of metal ions, nitro-explosives, drugs and contaminants in industrial wastes.

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