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Metal–Organic Frameworks with Pyridyl-Based Isophthalic Acid and Their Catalytic Applications in Microwave Assisted Peroxidative Oxidation of Alcohols and Henry Reaction

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Abstract

Reactions of 5-{(pyridin-4-ylmethyl)amino} isophthalic acid (H_2L1) with copper(II), zinc(II) and cadmium(II) were studied and the obtained MOFs $[\{Cu(L1)(DMF)\}.DMF.H_2O]_n$ (**1**), $[Zn(L1)(H_2O)]_n$ (**2**) and $[Cd(L1)]_n$ (**3**) were characterized by elemental analysis, FT-IR spectroscopy and X-ray single-crystal diffraction. As shown by X-ray crystallography, novel hybrid organic–inorganic coordination-driven assemblies were obtained which exhibit different two and three dimensional polymeric architectures. Compounds **1** and **2** have 2D structures whereas compound **3** features a 3D network type polymer with a dimetallic core act as a secondary building unit. These frameworks act as heterogeneous polymeric solid catalysts (the most effective one being the copper MOF **1**) for solvent-free microwave assisted peroxidative oxidation of primary and secondary alcohols. They also effectively catalyze the nitroaldol (Henry) reaction of different aldehydes with nitroalkanes in water. These MOF-based heterogeneous catalysts are of easy recovery and reused, at least for a few consecutive cycles, without losing activity.

Keywords: Metal Organic Frameworks, Crystal Structure analysis, Heterogeneous Catalysis, Alcohol oxidation, Microwave-assisted catalysis, Nitroaldol (Henry) reaction

Introduction

Metal–organic frameworks are compounds consisting of inorganic metal ions and organic linkers, which have attracted a significant interest recently.[1-9] The rapid development in this field is due to their attractive structures and topologies, as well as to their uses in various areas, *e.g.*, catalysis,[10-12] nonlinear optics,[13] gas storage and separation,[14] and magnetism.[15] However, the construction of multi-dimensional coordination frameworks is still challenging. The reactivity and solubility of the linkers and the choice of ligands with adequate binding centres play an important role in the suitable construction of MOFs.[16] In recent years a marked improvement in the synthesis of porous MOFs with multidentate aromatic carboxylate ligands has been accomplished.[17-18]

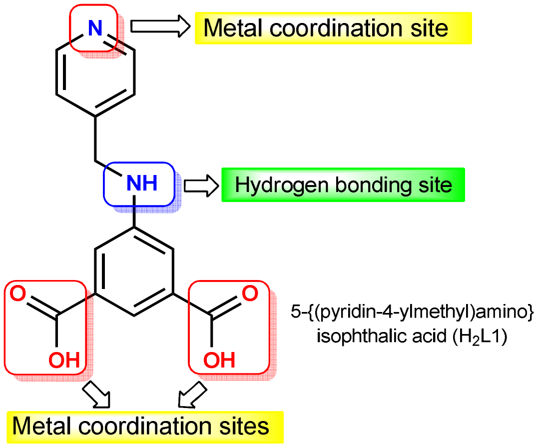
Primary and secondary alcohols oxidations are relevant in modern organic chemistry.[19-22] Many different metal catalysts have been reported for this reaction but most of them are homogeneous.[23-24] It is also important to try to develop new catalytic oxidation procedures using green oxidants, such as O_2 or peroxides [H_2O_2, *tert*-butylhydroperoxide (TBHP)], namely to overcome the formation of harmful wastes.[25,26]

Moreover, the use of solvent-free conditions,[27] of ecofriendly and efficient catalysts and green oxidants, and of microwave (MW) irradiation (with eventual advantages over traditional heating,[28,29] *e.g.*, a shorter reaction time and higher product yield and selectivity) is also promising. Efficient copper(II)[30-33] and iron(III)[34-35] catalytic systems have been recently achieved by us, for aerobic and peroxidative (with TBHP) oxidations of various primary and secondary alcohols, namely involving a solvent-free MW procedure. However, most of our reported catalysts are homogenous, and thus it would be desirable to spread our work to heterogeneous ones. Moreover, only a few MOFs are known as heterogeneous catalysts for alcohols oxidation,[36] and numerous challenges and opportunities still remain. Thus, MOF based heterogeneous catalysts with higher stability and activity, and easier accessible metal centres are worth developing.

The Henry or nitroaldol reaction provides an interesting C–C bond formation method in modern organic chemistry.[37,38] Generally, this reaction is effectively catalyzed by basic catalysts, like alkali metal hydroxides, alkoxides or amines.[39] Recently, some MOFs and discrete complexes were reported by our group to catalyze this reaction efficiently.[40-45] Nevertheless, it is still challenging to develop new types of heterogeneous catalysts based on MOFs, displaying a high activity under mild conditions and able to recycling.

In this context, we have chosen 5-{(pyridin-4-ylmethyl)amino}isophthalic acid (H_2L1) as an organic ligand/ linker due to the following features: (a) easy tuning of the extent of deprotonation of the carboxylic groups by changing the pH of the reaction medium, with expected formation of multidimensional MOFs; (b) flexibility of the pyridyl arm of H_2L1, able to adopt various conformations, with possible formation of various architectures; (c) introduction of an amine functionality in H_2L1 which can offer additional hydrogen bonding sites, as well as a Lewis-basic nature to the frameworks (Scheme 1). Recently, various MOFs with interesting architectures and properties have been synthesized using similar types of ligands.[46-50]

Therefore, the objectives of this study are the following: (i) design, preparation and characterization of different multi-dimensional MOFs using H_2L1 as a linker; (ii) application of the synthesized frameworks as heterogeneous catalysts for MW promoted and solvent free oxidation of primary and secondary alcohols with a peroxide oxidant and for the Henry reaction of aldehydes with nitroalkanes in a green solvent; (iii) achievement of a catalyst that would be effective in a sequential catalytic conversion of alcohols to aldehydes followed by the conversion of the latter into nitroalkanes. In accord, by using H_2L1 as a pro-ligand, we report the preparation of $[\{Cu(L1)(DMF)\}.DMF.H_2O]_n$ (**1**), $[Zn(L1)(H_2O)]_n$ (**2**) and $[Cd(L1)]_n$ (**3**) MOFs, their syntheses, characterization and heterogeneous catalytic activities towards the solvent-free microwave assisted alcohol (primary and secondary) oxidation and the nitroaldol reaction of aldehydes.



Scheme 1

Experimental Section

All the chemicals in the current study were purchased from commercial sources and utilized without further purifications. A Bruker Vertex 70 instrument was used for the IR (4000–400 cm^{-1}) measurements of samples prepared as KBr pellets; abbreviations: s = strong, m = medium, w = weak, bs = broad and strong, mb = medium and broad. Elemental analyses of all compounds were performed at the Microanalytical Service of the Instituto Superior Técnico. Powder X-ray diffraction (PXRD) was conducted in a D8 Advance Bruker AXS (Bragg Brentano geometry) theta-2theta diffractometer, with copper radiation (Cu Kα, λ = 1.5406 Å) and a secondary monochromator, operated at 40 kV and 40 mA. Flat plate configuration was used and the typical data collection range was between 5° and 40°.

5-{(pyridin-4-ylmethyl)amino}isophthalic acid (H_2L1) was synthesized according to the reported procedure[48] in an open atmosphere under air, while the metal organic frameworks were prepared under hydrothermal conditions.

Synthesis of $H_3L1^+Cl^-$

To a H_2L1 (27.0 mg, 0.10 mmol) solution in methanol (2.0 mL) was added 1 drop of conc. HCl, whereupon the system was stirred (30 min) and kept for crystallization. After 2 days block shape colourless crystals were obtained. Anal. Calcd. for $C_{14}H_{13}ClN_2O_4$ (*M* = 308.06): C, 54.47; H, 4.24; N, 9.07; Found: C, 54.60; H, 4.16; N, 9.11. FT-IR (KBr, cm^{-1}): 3315 (bs), 3072 (bs), 1720 (s), 1613 (s), 1506 (s), 1446 (m), 1326 (m), 1262 (m), 1227 (m), 1136 (w), 1032 (m), 921 (m), 824 (s), 761 (s), 678 (s), 469 (m), 437 (m).

Synthesis of 1

A solution of $Cu(NO_3)_2.3H_2O$ (24.0 mg, 0.10 mmol) and H_2L1 (27.0 mg, 0.10 mmol) in DMF (2.0 mL) was stirred at room temperature for 30 min, whereupon 1 mL of 28% aqueous solution of NH_4OH was added into it. The resulting clear dark blue solution was left at room temperature for 3 days leading to precipitation of block-like deep green crystals. Yield: 77% (based on Cu). Anal. Calcd. for $C_{20}H_{26}CuN_4O_7$ (*M* = 497.99): C, 48.24; H, 5.26; N, 11.25; Found: C, 48.00; H, 5.07; N, 11.12. FT-IR (KBr,

cm^{-1}): 3352 (bs), 1616 (s), 1558 (s), 1426 (s), 1405 (s), 1363 (s), 1243 (w), 1065 (w), 1032 (w), 969 (w), 879 (w), 781 (s), 729 (s), 561 (w).

Synthesis of 2

To an equivalent molar (1:1) solution (5 mL) of H_2L1 (27.0 mg, 0.10 mmol) and $Zn(NO_3)_2.6H_2O$ (29.0 mg, 0.10 mmol) in DMF and methanol (1 : 1) was added 0.5 mL of 28% aqueous ammonia. A white precipitate formed but it was dissolved by further addition of the same amount (0.5 mL) of that solution. Then, the resulting solution was transferred and sealed in an 8 mL glass vessel and heated (hydrothermal reactor) at 75 ˚C for 48 h. Subsequent cooling of that solution to room temperature (0.2 ˚C min^{-1}) afforded plate-like colorless crystals of **2**. Yield: 68% (based on Zn). Anal. Calcd. for $C_{17}H_{19}N_3O_6Zn$ (*M* = 426.73): C, 47.85; H, 4.49; N, 9.85; Found: C, 47.63; H, 4.31; N, 9.45. FT-IR (KBr, cm^{-1}): 3413 (bs), 1619 (s), 1567 (s), 1407 (s), 1384 (s), 1244 (w), 1148 (w), 1065 (w), 1031 (w), 972 (w), 914 (w), 778 (s), 732 (s), 536 (w).

Synthesis of 3

A solution of $Cd(NO_3)_2.4H_2O$ (31.0 mg, 0.10 mmol) and H_2L1 (27.0 mg, 0.10 mmol) in 5 mL of DMF: 1,4-dioxane: water (2 : 2: 1) mixture was prepared and then transferred and sealed in an 8 mL glass vessel, and heated (hydrothermal reactor) at 75 ˚C for 48 h. Subsequent cooling of that solution to room temperature (0.2 ˚C min^{-1}) afforded plate-like colorless crystals of **3**. Yield: 71% (based on Cd). Anal. Calcd. for $C_{19}H_{21}CdN_3O_6$ (*M* = 499.80): C, 45.66; H, 4.24; N, 8.41; Found: C, 45.39; H, 4.15; N, 8.12. FT-IR (KBr, cm^{-1}): 3412 (bs), 1653 (m), 1604 (s), 1556 (s), 1441 (m), 1423 (m), 1382 (s), 1253 (w), 1107 (w), 1061 (w), 1041 (w), 968 (w), 783 (s), 735 (s), 682 (s), 570 (w).

Solvent-Free Microwave-Assisted Peroxidative Oxidation of Alcohols

The alcohol (2.5 mmol), the catalyst (5 µmol) and *t*-BuOOH (70% aqueous solution, 5 mmol) were introduced into a cylindrical Pyrex tube which was then sealed and placed into the focused Anton Paar Monowave 300 microwave reactor. The system was stirred and irradiated (5 W) at 100 ºC for 0.5 h. After the reaction, the system was allowed to cool down to room temperature. The internal standard (150 µL of benzaldehyde or cyclopentanone, respectively for secondary or primary alcohols) was added and then acetonitrile (2.5 mL to extract the substrate and the organic products from the reaction mixture). After stirring the mixture for 10 min, an aliquot (1 µL) from the organic phase was taken and analyzed by GC. Tests in the absence of catalysts were also undertaken under the above reaction conditions and no considerable alcohol conversion was detected.

In order to perform the recycling experiment, we have separate the solid catalyst **1** by hot filtration from the reaction mixture and dried overnight at 50º C. It was then used for next cycle of the oxidation reaction as described above.

Henry Reaction

To 2 mL water in a glass vessel was added a mixture of aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and catalyst (2 mol%, 9.9 mg for **1**, 8.5 mg of **2** and 10.0 mg of **3**) and the capped reaction system was heated at 75˚C. After the desired time the mixture was centrifuged to remove the solid catalyst and the separated solution was extracted with CH_2Cl_2. The extracts were dried over anhydrous Na_2SO_4, whereupon evaporation of the solvent gave the crude product which was analyzed by ^1H NMR after dissolving in DMSO-d^6. The β-nitroalkanol yield and the corresponding *syn*/*anti* selectivity were estimated following our published procedure.[44] The product isomers were identified by ^1H NMR (Figure S3, supporting information). The values of vicinal coupling constants between the α-N–C–H and the α-O–C–H protons characteristic of the isomers are as follows: *J* = 7–9 or 3.2–4 Hz for the *syn* or *anti* isomers, respectively.[51]

The recycling experiments were performed after washing and drying the used catalyst at room temperature. The rest of the procedure was followed as indicated above.

Crystal Structure Determinations

X-ray quality single crystals of the compounds were mounted in a nylon loop and their intensity data were collected using a Bruker AXS-KAPPA APEX II or a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71069) radiation at 150 K (**2**) or at room temperature (**1**, **3** and $H_3L1^+Cl^-$). Cell parameters were retrieved and refined using Bruker SMART[52-54] and Bruker SAINT[52] softwares, respectively. Absorption corrections were made using SADABS.[52] Structures were solved and refined using the SHELXS-97[53] with SHELXL-97[53] packages, respectively. Calculations were performed using the WinGX System–Version 1.80.03.[54] The hydrogen atoms attached to carbon atoms and to the nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2Ueq of the parent nitrogen atoms or the carbon atoms for phenyl and methylene residues, and 1.5Ueq of the parent carbon atoms for the methyl groups. The hydrogen atoms of coordinated water molecules were located from the final difference Fourier map and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the belonging oxygen atoms. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed. PLATON/SQUEEZE[55] was used to correct the data and in framework **3** the potential volume of 1872 Å^3 was found with 494 electrons per unit cell worth of scattering. The electron count suggests the presence of *ca.* one dimethylformamide and two water molecules per asymmetric unit. The elemental analysis also supports these results. Crystallographic data are summarized in Table S1 (Supplementary Information file) and selected bond distances and angles are presented in Table S2. CCDC 1419063-1419066 for **1**-**3** and $H_3L1^+Cl^-$, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

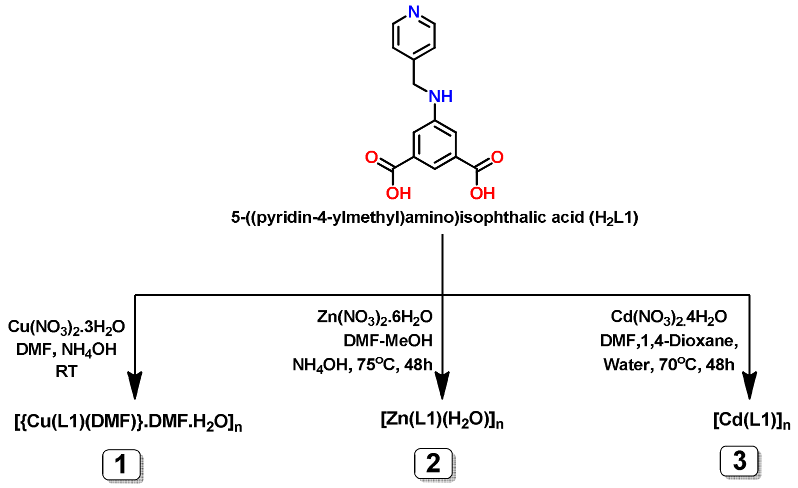
Results and Discussion

Syntheses and Characterization

The dicarboxylic acid ligand 5-{(pyridin-4-ylmethyl)amino}isophthalic acid (H_2L1) was synthesized according to the procedure reported earlier.[48]

We have used solvothermal reaction procedures for the syntheses of the frameworks **2** and **3,** but room temperature synthesis for **1**. The reaction of copper(II) nitrate with H_2L1 in the presence of dimethyl formamide (DMF) and NH_4OH leads to the formation of $[\{Cu(L1)(DMF)\}.DMF.H_2O]_n$ (**1**). The hydrothermal reaction of H_2L1 with zinc(II) nitrate hexahydrate in the presence of DMF-methanol and ammonium hydroxide forms $[Zn(L1)(H_2O)]_n$ (**2**), whereas the reaction with $Cd(NO_3)_2.4H_2O$ in

DMF, 1,4-dioxane and water mixture produces $[Cd(L1)]_n$ (**3**) [L1 = 5-{(pyridin-4-ylmethyl)amino}isophthalate] (Scheme 2).



Scheme 2

In the IR spectra of **1**-**3**, the characteristic strong bands of the coordinated carboxylate groups appear at 1604–1619 cm^{-1} for the asymmetric stretching and 1363-1384 cm^{-1} for the symmetric one.[7] The C–O stretching of coordinated carboxylate group is observed between 1243 and 1253 cm^{-1}. For H_2L1 the strong band at 1720 cm^{-1} is due to ν(CO) of uncoordinated carboxylic acid groups,[56] whereas ν(NH) of the amine group appears at 3072 cm^{-1}. Due to their insolubility in common NMR solvents, these frameworks were only characterized by single crystal X-ray diffraction and elemental analyses.

Crystal Structure Analyses

The single crystal X-ray analysis of **1** reveals that it crystallizes in the monoclinic $P2_1/n$ space group and is a bilayer type two dimensional framework constructed by Cu(II) ions and deprotonated $L1^{2-}$ ligands. The asymmetric unit contains a Cu^{2+} ion, one deprotonated ligand ($L1^{2-}$) and the coordinated DMF, as well as one of non-coordinated DMF and water molecules (Figure 1A). The Cu(II) centre has a distorted trigonal bipyramidal (τ_5 = 0.32)[57] geometry, the equatorial positions being occupied by three carboxylate oxygens from two $L1^{2-}$ ligands [Cu1–O1, 2.464 (3) Å, Cu1–O2, 1.963(2) Å and Cu1–O3, 1.936(2) Å] and the axial positions being coordinated by one DMF and one pyridyl-N groups [Cu1–O5, 1.979(3) Å and Cu1–N2, 2.000(3) Å] (Figure 1B). Selected bond distances and angles of **1** are listed in Table S3 (supporting information). The organic ligand is not planar, the isophthalate and pyridyl parts being almost perpendicular to each other with the angle of 84.11° and the C7-N1-C9-C10 torsional angle of -69.32°. Each $L1^{2-}$ ligand coordinates to three copper(II) ions and one carboxylate coordinates in a monodentate fashion while the other one chelates in a bidentate mode. In **1**, the distance between two neighbouring copper(II) ions is 8.5869(9) Å**.** The 2D polymeric architecture of **1** also has open channels with approximate dimension of 7.59 x 7.00 Å^2, which are occupied by the non-coordinated water and DMF molecules (Figure 1C).

The non-coordinated water and DMF molecules are stabilized by a number of hydrogen bonding interactions. These involve the hydrogens of a non-coordinated water molecule O7 (as donor) and the carboxylate oxygen O4 (as bifurcated acceptor). The amine NH- is also involved in hydrogen bonding with carboxylate oxygen via N1-H1A···O1 ($d_{D–A}$ 2.961(4) Å; <D–H····A 171˚) interaction. Relevant hydrogen bond distances and angles are listed in Table S2 (supporting information). Moreover, a number of C–H···O interactions are present in this structure which helps its expansion to the third dimension (Figure 1D).

Single crystal X-ray analysis reveals that the 2D framework **2** crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains a Zn^{2+} ion, one deprotonated ligand ($L1^{2-}$) and one coordinated water molecule (Figure 2A).

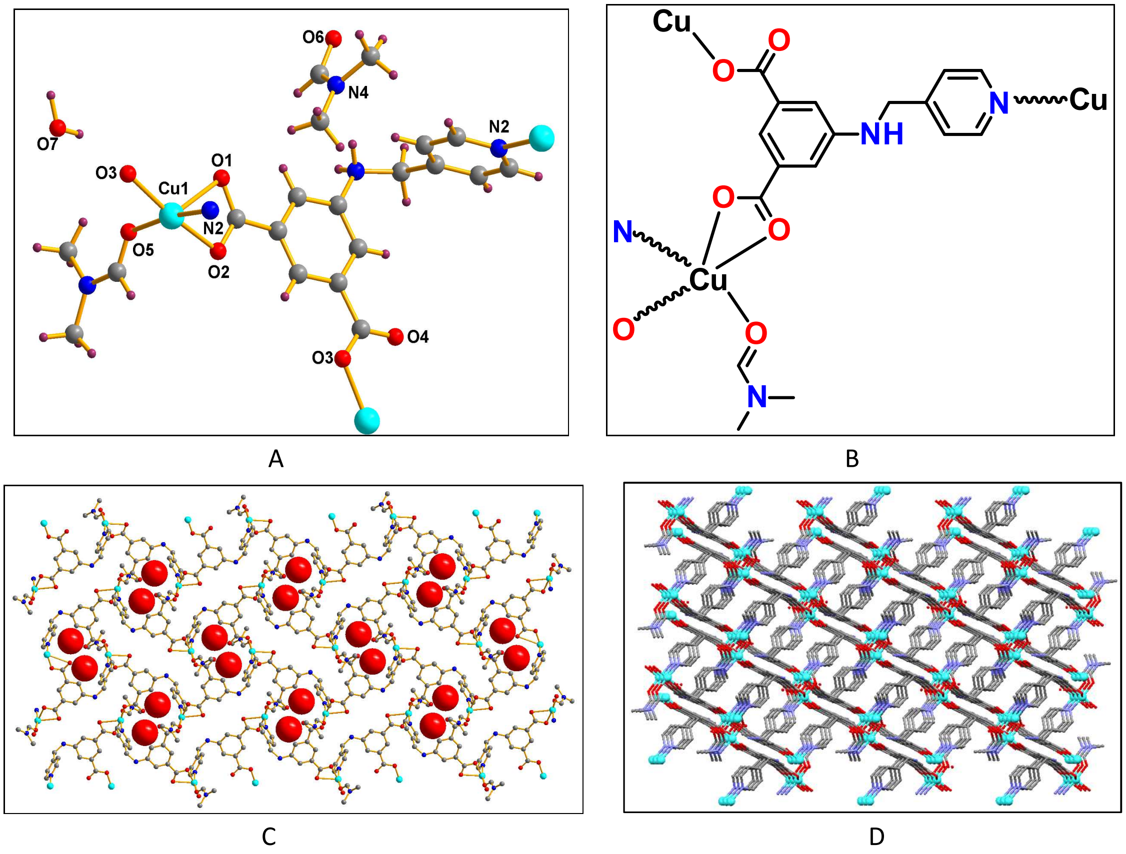
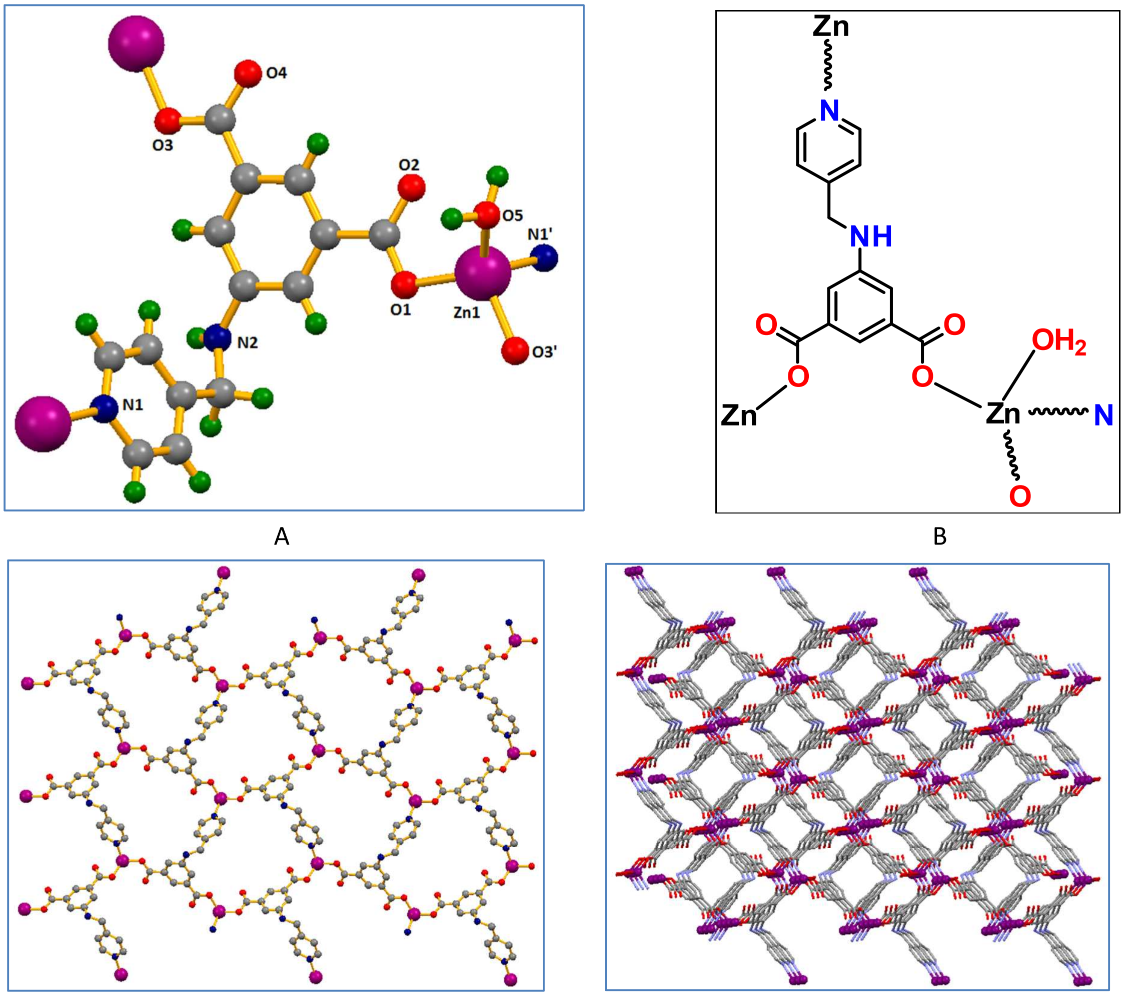


Figure 1: (A) The asymmetric unit of framework **1** with partial atom labelling scheme. (B) Schematic representation of the asymmetric unit of **1**. (C) Two dimensional structure of framework **1** (water molecules are indicated as red balls). (D) Three dimensional packing view of framework **1**.

The Zn(II) ion has a tetrahedral (τ_4 = 0.91)[58] coordination geometry occupied by two monodentate carboxylate oxygens from two $L1^{2-}$ ligands [Zn1–O1, 1.973(2) Å and Zn1–O3, 1.974(2) Å], one water molecule [Zn1–O5, 1.985(4) Å] and one pyridyl-N of $L1^{2-}$ ligand [Zn1–N1, 2.050(3) Å] (Figure 2B). Selected bond distances and angles are listed in Table S3 (supporting information). The minimum Zn···Zn distance reaches 10.3492(8) Å. The $L1^{2-}$ ligand is not planar, the isophthalate and pyridyl part almost perpendicular with the angle of 80.12° and the C4-N3-C8-C9 torsional angle of 76.43°. A close inspection of the 2D structural arrangement in **2** indicates that the metals are assembled via bridging oxygen atoms in one dimensional chains. These chains are then interconnected by the pyridyl-N of $L1^{2–}$ ligand giving rise to a 2D square grid type framework with the approximate dimension of 10.7 X 11.0 Å^2 that runs diagonally along the crystallographic *ac*-plan (Figure 2C). The framework **2** contains a void space of 27.5% per unit cell according to PLATON.[55] Moreover, the intermolecular organization in the crystal is characterized by hydrogen bonding interactions involving the carboxylate groups as acceptors and the coordinated water molecule as donor, expanding the structure to the third dimension (Figure 2D, Table S2).



A

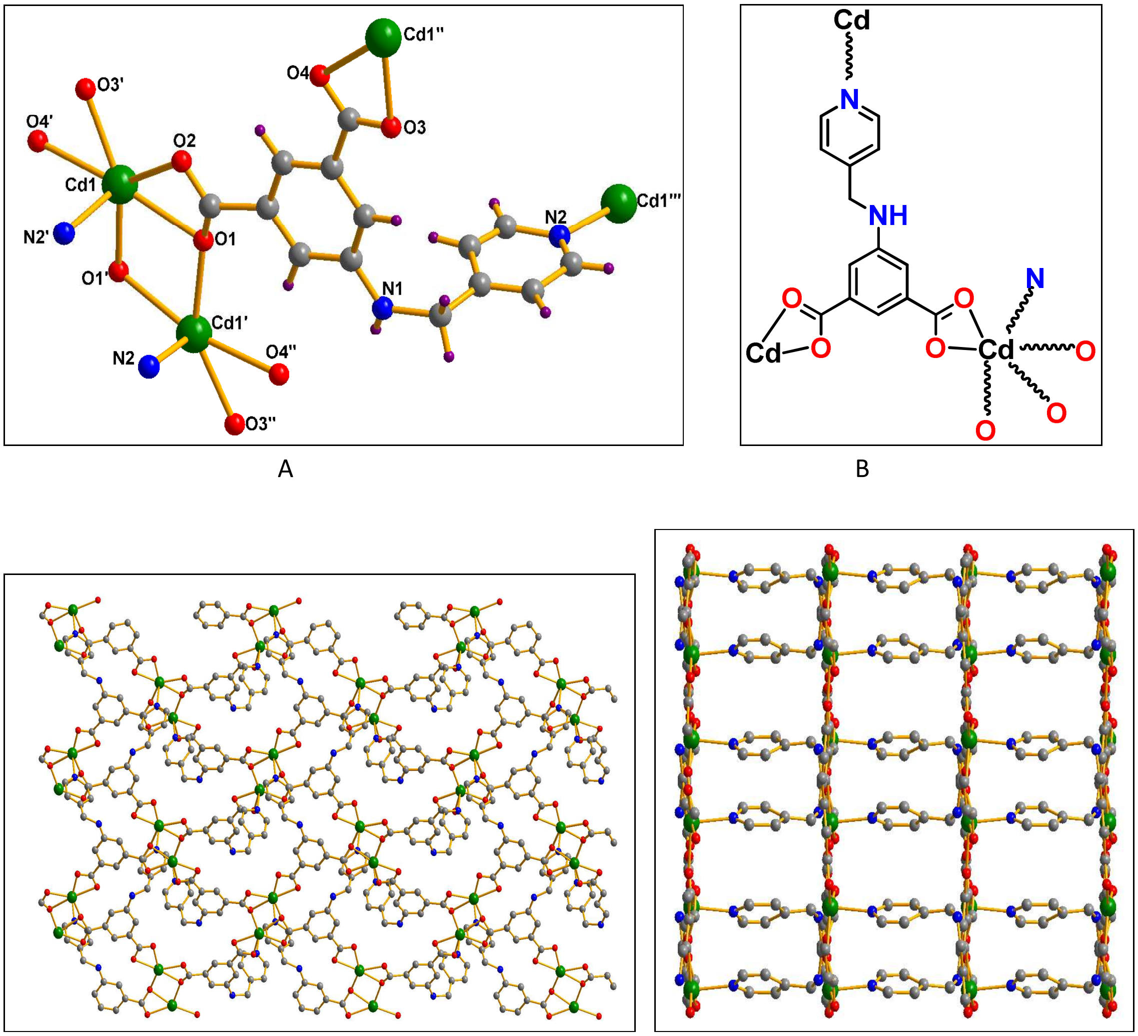
B

C

D

Figure 2: (A) The asymmetric unit of framework **2** with partial atom labelling scheme. (B) Schematic representation of the asymmetric unit of **2**. (C) Two dimensional structure of framework **2**. (D) Three dimensional packing view of framework **2**.

The single crystal X-ray analysis of **3** reveals that it is a three dimensional framework constructed by Cd(II) ions and deprotonated L1^{2-} ligands which crystallize in the orthorhombic Aba2 space group. The asymmetric unit contains a Cd^{2+} ion and one deprotonated L1^{2-} ligand (Figures 3A and 3B). The Cd(II) ion has a hexa-coordinated geometry where five coordination sites are occupied by five carboxylate oxygen atoms from three neighbouring L1^{2-} ligands [Cd1-O1, 2.385(4); Cd1-O2, 2.354(5); Cd1-O3, 2.344(4); Cd1-O4, 2.463(4); Cd1-O1', 2.475(4)] and the remaining position is coordinated axially by one pyridyl-N group [Cd1-N2, 2.311(5)] (Figure 3B). Selected bond distances and angles are listed in Table S3 (supporting information). In this framework, the L1^{2-} is bent and the pyridyl group is almost perpendicular to the isophthalate group as observed in the previous complexes. The angle between them is 89.00° and the C4-N1-C9-C10 torsional angle is -79.69°. In the ligand $L1^{2-}$, one carboxylate coordinates to a single metal center in a chelating fashion whereas the other carboxylate group coordinates two different Cd(II) ions via a μ_2-chelating mode. In this framework a dinuclear Cd(II) cluster acts as a secondary building block unit. Each dinuclear unit is coordinated by six different $L1^{2-}$ ligands whereas each $L1^{2-}$ ligand connected with four different Cd(II) ions. The Cd(II) ions are assembled via bridging carboxylate oxygen atoms in a two dimensional chain and these chains are further interconnected by the pyridyl-N giving rise to 3D framework. This 3D polymeric architecture of **3** also has some open channels with approximate dimension of 9.4 X 6.6 Å^2 (Figures 3C and 3D) and a void space of 45.5% per unit cell according to PLATON[55] after removing the non-coordinated solvent molecules. Moreover, a number of C–H···O interactions are present in this structure helping its stabilization.



A

B

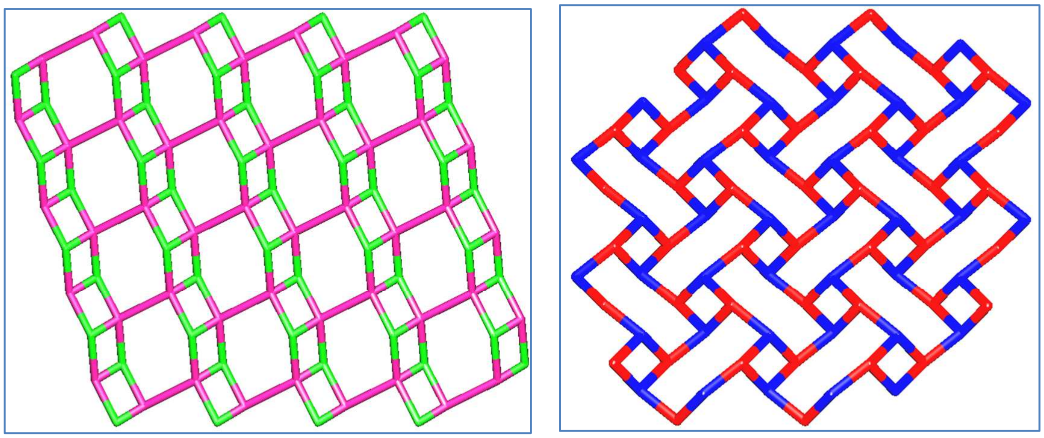
C

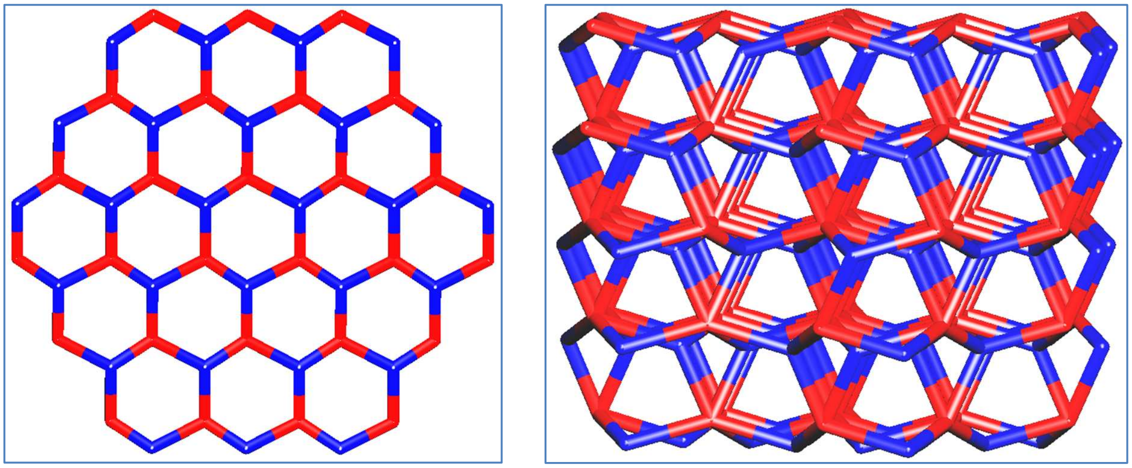
D

Figure 3: (A) The asymmetric unit of framework **3** with partial atom labelling scheme. (B) Schematic representation of an asymmetric unit of **3**. (C) Three dimensional structure of framework **3**. (D) View of packing diagram of **3** along *a*-axis.

It is worth mentioning that this ligand has previously been utilized to synthesize a few 3D polymers of manganese(II) by Bharadwaj *et el.*[48,49] The ligand therein is coordinated to four Mn(II) centres to form catena-(bis(μ_4-5-((pyridin-4-ylmethyl)amino)isophthalato)-mono/di-manganese(II) polymers whereas in our cases (**1**-**3**) it connects three metal centres to yield catena-(bis(μ_3-5-((pyridin-4-ylmethyl)amino)isophthalato) polymers.

To improve the description of the crystal structures of **1-3** we performed their topological analysis by reducing their multidimensional structures to simple node-and-linker nets where the metallic nodes and the organic linkers represent secondary building units (SBUs). We have carried out these analyses by using TOPOS 4.0.[59] In the particular case of $H_3L1^+Cl^-$, each protonated H_3L1^+ unit is hydrogen bonded with four different H_3L1^+ and each Cl^- anion is halogen bonded with three different H_3L1^+. $H_3L1^+Cl^-$ represents a 3,4-connected 2-nodal net with the topological type 3,4L83 (Figure 4A). Topological analysis of framework **1** reveals that it has a 3-connected uninodal net with a topological type fes (Shubnikov plane net) and point symbol (4.8^2) (Figure 4B). Similarly, framework **2** has also 3-connected uninodal net with a topological type hcb (Shubnikov hexagonal plane net) and the point symbol (6^3) (Figure 4C). In case of framework **3**, we have considered the dinuclear Cd(II) unit as a single node and connected with six different $L1^{2-}$ ligands and each ligand connected with three Cd(II) centres. Thus, framework **3** represents a 3,6-connected binodal net structure with topological type flu-3,6-I41cd (Figure 4D).



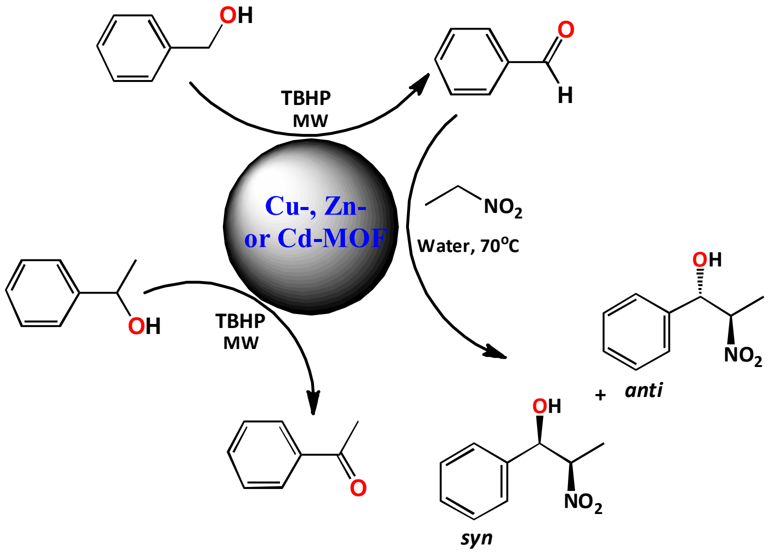


C D

Figure 4 Node-and-linker-type descriptions of: (A) the 2D hydrogen bonded frameworks in $H_3L1^+Cl^-$ (H_3L1^+ represented in pink color and Cl^- in green color); (B) the 2D coordination frameworks in **1**; (C) the 2D coordination framework in **2**; (D) the 3D coordination frameworks in **3**. The metal nodes are represented in red color and the carboxylate linker in blue color.

Catalytic applications of MOFs

Compounds **1**–**3** are catalysts for the solvent-free microwave (MW) assisted oxidation of primary or secondary alcohols (benzyl alcohol or 1-phenylethanol as model substrates) to the corresponding aldehydes or ketones as well as for the nitroaldol (Henry) reaction between several benzaldehydes and nitroalkanes (Scheme 3).



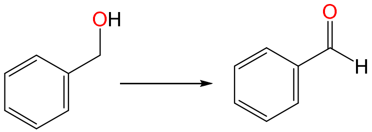
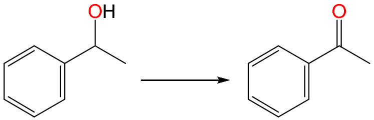
Scheme 3

In Oxidation of Alcohols

Compounds **1**–**3** were tested as heterogeneous catalysts for the solvent-free microwave (MW) assisted oxidation of benzyl alcohol or 1-phenylethanol to benzaldehyde or acetophenone, respectively, with aqueous *tert*-butyl hydroperoxide (^{t}BuOOH, TBHP, aq. 70%, 2 eq) as oxidizing agent (Scheme 3), at 100 ºC typically during 0.5 h of irradiation.

The optimized results, in terms of yield, selectivity and turnover frequency (TOF, moles of product/mol of catalyst per hour), are presented in Table 1. Benzaldehyde or acetophenone is the only product detected in the assayed conditions for the oxidation of benzyl alcohol or 1-phenylethanol, respectively. The best results were obtained with the copper(II)-based MOF **1** (Table 1, entries 1 and 7, respectively). Under the above conditions, 81 or 98% yield of benzaldehyde or acetophenone and TOF of 811 or 983, respectively, are obtained in the absence of any additive. The reactions performed under the same conditions but in the presence of the other MOFs resulted in much lower yields (between 13 and 19%, Table 1) and TOFs (between *ca.* 130 and 190, Table 1) in benzaldehyde or acetophenone.

Table 1. Selected data[a] for the solvent-free MW-assisted oxidation of benzyl alcohol and 1-phenylethanol using **1** - **3** as catalysts.

<table>
<tr><td colspan="5">
</td></tr>
<tr><td>Entry</td><td>MOF or precursor salt</td><td>Yield[b] /%</td><td>TOF[c] /h^{-1}</td><td>Select[d] /%</td></tr>
<tr><td>1</td><td>**1**</td><td>81.1</td><td>811</td><td>>99</td></tr>
<tr><td>2</td><td>$Cu(NO_3)_2.3H_2O$</td><td>17.2</td><td>172</td><td>77</td></tr>
<tr><td>3</td><td>**2**</td><td>15.3</td><td>153</td><td>99</td></tr>
<tr><td>4</td><td>$Zn(NO_3)_2.6H_2O$</td><td>6.8</td><td>68</td><td>66</td></tr>
<tr><td>5</td><td>**3**</td><td>12.8</td><td>128</td><td>98</td></tr>
<tr><td>6</td><td>$Cd(NO_3)_2.4H_2O$</td><td>5.9</td><td>59</td><td>85</td></tr>
<tr><td colspan="5">
</td></tr>
<tr><td>7</td><td>**1**</td><td>98.3</td><td>983</td><td>>99</td></tr>
<tr><td>8</td><td>$Cu(NO_3)_2.3H_2O$</td><td>23.1</td><td>231</td><td>67</td></tr>
<tr><td>9</td><td>**2**</td><td>19.2</td><td>192</td><td>>99</td></tr>
<tr><td>10</td><td>$Zn(NO_3)_2.6H_2O$</td><td>8.3</td><td>83</td><td>74</td></tr>
<tr><td>11</td><td>**3**</td><td>16.1</td><td>161</td><td>99</td></tr>
</table>

12	$Cd(NO_3)_2.4H_2O$	3.9	39	81

[a] Reaction conditions: 2.5 mmol of benzyl alcohol or 1-phenylethanol, 5 µmol (0.2 mol % *vs*. substrate) of **1** - **3**, 5 mmol of TBHP (2 equiv, 70 % in H_2O), T = 100 ºC, t = 0.5 h, MW irradiation (5 W power). [b]Moles of benzaldehyde or acetophenone per 100 moles of alcohol substrate. [c] Number of moles of benzaldehyde or acetophenone per mole of catalyst per hour. [d] Moles of benzaldehyde or acetophenone per mole of converted substrate.

Blank tests were performed under the same reaction conditions but in the absence of MOFs and no significant conversion of benzyl alcohol or 1-phenylethanol was observed. Moreover, the replacement of **1** - **3** by their precursor salts, $M(NO_3)_2.xH_2O$ (M = Cu, Zn or Cd; x =3, 6 or 4), resulted in a drastic decrease of activity (compare *e.g.*, entries 1 and 2, Table 1) suggesting a significant role of the ligand L1 in the catalytic oxidation of the tested alcohols. The reaction catalyzed by the most active compound (**1**) appears to proceed mainly *via* a radical mechanism, which involves oxygen- and carbon-radicals since a strong inhibiting effect on the catalytic activity was observed upon addition, to the reaction mixture, of Ph_2NH or $CBrCl_3$, well known[60] oxygen- or carbon-radical traps, respectively. The benzaldehyde yield decreased from 81% (entry 1, Table 1) to 3.8% or 1.3%, respectively, in the presence of Ph_2NH or $CBrCl_3$. Similarly, the formation of acetophenone (98% yield, entry 7, Table 1) catalyzed by **1** was significantly reduced to 2.6% or 2.9%, respectively, when Ph_2NH or $CBrCl_3$ was added to the reaction medium. Hence, the oxidation mechanism may involve the metal-assisted generation of radicals $^t\mathrm{BuOO}^\bullet$ (upon oxidation of ^{t}BuOOH by a Cu(II) centre) and $^t\mathrm{BuO}^\bullet$ (upon reduction of ^{t}BuOOH by the formed Cu(I) centre), which behave as hydrogen atom abstractors from the alcohols. The mechanism conceivably is similar to those proposed in other cases, which are also of a radical type.[61,62] The ligand L1 can assist proton transfer steps involved in the fundamental steps of the above reaction,[61,62] improving the catalytic activity of its complexes.

The present system, in particular in the presence of **1**, leads to much higher yields of oxidized products in an exceptionally short reaction time compared with those reported for MW-assisted[32,33] or conventional heating[63] peroxidative oxidations of secondary alcohols or TEMPO-assisted aerobic oxidations of primary alcohols[64-70] in the presence of other metallic MOFs. Moreover, our catalytic system exhibits good activity for both primary and secondary alcohols, a feature that is also noteworthy. For example, it was found[67,68] that copper MOFs based on carboxylate ligands, $[Cu_3(BTC)_2]$ (BTC = 1,3,5-benzenetricarboxylate), which are able to catalyze the TEMPO-assisted aerobic oxidation of benzyl alcohol (leading to 99% yield of benzaldehyde after 16 h reaction at 70 ºC[67] or to 100% yield of benzaldehyde after 10 h if used as mesocellular MOFs[68]), are not effective when applied to the aerobic oxidation of secondary alcohols, such as 1-phenylethanol or benzhydrol.[67]

In Henry Reaction

We have also tested the catalytic activity of compounds **1**-**3** as solid heterogeneous catalysts in the nitroaldol (or Henry) reaction of nitroethane with various aldehydes. Previously, we have reported various Zn(II) and Cu(II) coordination polymers and complexes which are significantly active for such a type of reaction.[40-45] In **1**-**3**, the presence of amine group (which can promote the reaction) and the structural rigidity (which can improve the selectivity) encouraged us to apply them to such a reaction.

By using benzaldehyde as a test compound, we have found that **1** showed a higher activity than the other frameworks, after the same reaction time and at the same temperature. Consequently, the optimization of the reaction conditions (temperature, reaction time, amount of catalyst and solvent) was carried out in a model nitroethane–benzaldehyde system with catalyst **1** (Table 2).

A blank test was carried out with benzaldehyde in the absence of any metal catalyst, at 75˚C in water. No considerable amount of β-nitroalkanol was detected after a reaction time of 40 h. The nitroaldol reaction also did not take place by using compound H_2L1 instead of the metal catalyst (Table 2, entry 23). We have also checked the reactivity of $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$ and $Cd(NO_3)_2.4H_2O$ in water medium and the obtained reaction yields are in the range of 9-14% (entries 20-22, Table 2), much lower than those achieved in the presence of the MOF.

When 2 mol% of **1** is used as catalyst, a conversion of 84% (*syn*:*anti* = 82:18) of benzaldehyde into β-nitroalkanol is reached (entry 7, Table 2). With **2** and **3**, conversions of 71% (*syn:anti* = 81:19) and 69% (*syn:anti* = 79:21) were obtained, respectively (entries 17-18, Table 2). Extending the reaction time to 48 h did not increase the yield of the reaction. The plot of yield *versus* time for the Henry reaction of benzaldehyde and nitroethane with framework **1** is presented in Figure 5.

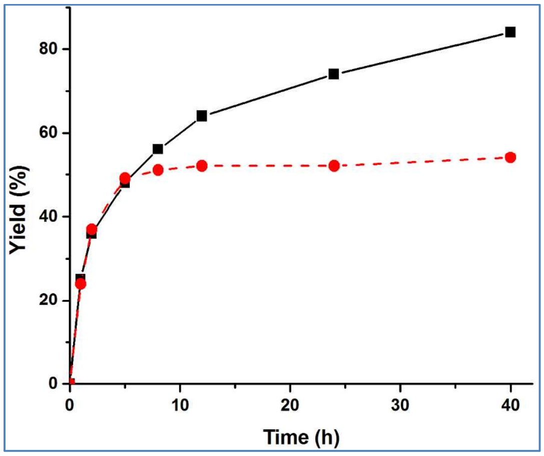
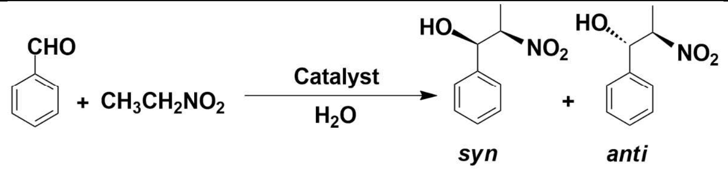


Figure 5 Plot of β-nitroalkanol yield *vs.* time for the Henry reaction of benzaldehyde and nitroethane in presence of catalyst **1** (black curve) and after filtering off the catalyst **1** (red curve).

Table 2. Optimization of the parameters of the Henry reaction between benzaldehyde and nitroethane with **1** as the catalyst[a]



Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	*T* (˚C)	Solvent	Yield (%)[b]	Selectivity (*syn/anti)*[c]	TON[d]
1	**1**	1	2.0	75	H_2O	25	84:16	12
2	**1**	2	2.0	75	H_2O	36	79:21	18
3	**1**	5	2.0	75	H_2O	48	80:20	24
4	**1**	8	2.0	75	H_2O	56	82:18	28

5	**1**	12	2.0	75	H_2O	64	81:19	32
6	**1**	24	2.0	75	H_2O	74	81:19	37
7	**1**	40	2.0	75	H_2O	84	82:18	42
8	**1**	40	1.0	75	H_2O	56	79:21	56
9	**1**	40	3.0	75	H_2O	83	77:23	28
10	**1**	40	5.0	75	H_2O	84	78:22	17
11	**1**	40	2.0	75	THF	49	81:19	24
12	**1**	40	2.0	75	MeOH	78	76:24	39
13	**1**	40	2.0	75	CH_3CN	5	77:23	3
14	**1**	40	2.0	25	H_2O	15	85:15	7
15	**1**	40	2.0	50	H_2O	51	80:20	26
16	**1**	40	2.0	100	H_2O	77	75:25	38
17	**2**	40	2.0	75	H_2O	71	81:19	35
18	**3**	40	2.0	75	H_2O	69	79:21	34
19	Blank	40	-	75	H_2O	-	-	-
20	$Cu(NO_3)_2.3H_2O$	40	2.0	75	H_2O	11	82:18	6
21	$Zn(NO_3)_2.6H_2O$	40	2.0	75	H_2O	9	78:22	5
22	$Cd(NO_3)_2.4H_2O$	40	2.0	75	H_2O	14	80:20	7
23	H_2L1	40	2.0	75	H_2O	-	-	-

[a]Reaction conditions: 2.0 mol% of catalyst **1**, benzaldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and water (2.0 mL). [b] Number of moles of β-nitroalkanol per 100 moles of aldehyde. [c] Calculated by ^1H NMR. [d] Number of moles of β-nitroalkanol per mole of catalyst.

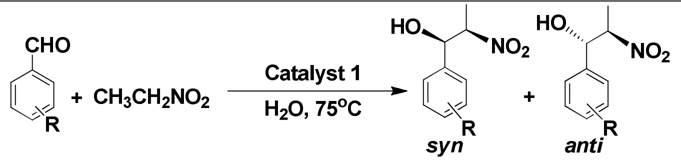
We have also tested the effect of catalyst amount, solvent and temperature. An increase of the catalyst amount from 1.0 and 2.0 mol% enhances the product yield from 56 to 84%, respectively (entries 8 and 7, Table 2), but a further rise of that amount did not improve the reaction yield (entries 9 and 10, Table 2).

To select the most suitable solvent, experiments with various solvents (CH_3CN, THF, MeOH and H_2O) have been carried out with catalyst **1** (entries 7 and 11–13, Table 2) and the results indicate that water (84% yield) is the best solvent, whereas the worst one is CH_3CN (5% yield). In methanol and THF, the yields of 78% or 49%, respectively, were obtained (entries 12 and 11, Table 2).

Ranging the temperature from 25 to 75˚C improved the yield of β-nitroalkanol from 15 to 84% (entries 7 and 14–15, Table 2) but further increase in the reaction temperature had a negative effect (entry 16, Table 2). The systems exhibit diastereoselectivity towards the *syn* isomer, typically leading to *syn*:*anti* molar ratios in the range of 85:15 to 77:23 using nitroethane as substrate.

We have also compared the activities of catalyst **1** in the reactions of a variety of substituted aromatic and aliphatic aldehydes with nitroethane, producing the corresponding β-nitroalkanols with yields ranging from 41 to 98% (Table 3). Aryl aldehydes bearing an electron-withdrawing group exhibit higher reactivities (Table 3, entries 1 and 3) as compared to those having electron-donating moieties (Table 3, entries 2 and 5-7), what may be related with an increase of the electrophilicity of the substrate in the former case.

Table 3. Henry reaction of various aldehydes and nitroethane with catalyst **1**[a]

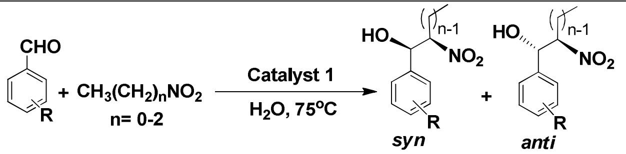


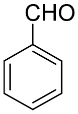
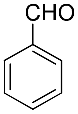
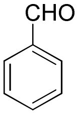
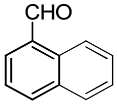
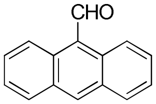
Entry	Aldehyde	Yield(%)[b]	Selectivity[c] (*syn*/*anti*)	TON[d]
1	4-Nitrobenzaldehyde	98	79:21	49
2	4-Methoxybenzaldehyde	41	82:18	21
3	4-Chlorobenzaldehyde	78	81:19	39
4	4-Hydroxybenzaldehyde	72	79:21	36
5	4-Methylbenzaldehyde	64	85:15	32
6	2-Methylbenzaldehyde	51	84:16	26
7	3-Methylbenzaldehyde	59	81:19	30
8	Acetaldehyde	90	82:18	45
9	Propionaldehyde	85	83:17	42

[a]Reaction condition: 2.0 mol% of catalyst **1**, aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and water (2.0 mL) at 75°C for 40 h. [b]Number of moles of β-nitroalkanol per 100 moles of aldehyde. [c] Calculated by ^{1}H NMR. [d] Number of moles of β-nitroalkanol per mole of catalyst.

To probe whether the catalytic reaction occurred inside the pores or on the surface of the solid catalyst, substrates of increasing dimensions were tested for **1**. We systematically varied the molecular sizes of nitrolalkanes [nitromethane (2.0 Å X 3.3 Å), nitroethane (2.2 Å X 3.9 Å) and nitropropane (2.2 Å X 5.6 Å)] and aldehydes [benzaldehyde (4.8 Å X 5.9 Å), naphthaldehyde (5.9 Å X 7.0 Å) and 9-anthraldehyde (6.0 Å X 9.3 Å)] to get an insight into the reaction mechanism and reaction centre. We have observed that the reaction yield systematically depends on the molecular size of the nitroalkanes and aldehydes. For example, when we have performed the reaction of benzaldehyde with nitropropane the yield was merely 42% compared with that of 91% for nitromethane (entries 3 and 1, Table 4). In the case of nitroethane, the yield was 84% (entry 2, Table 4). The yield decreased in the order of nitromethane (91%) > nitroethane (84%) > 1-nitropropane (42%). On the other hand, the reaction of benzaldehyde with nitroethane was accomplished with 84% yield after 40 h (entry 2, Table 4). In contrast, the yields for 1-naphthaldehyde and 9-antraldehyde (with molecular sizes that hamper their fitting in the catalyst cavities) are reduced to 45% and 29% under the same reaction conditions, respectively (entries 4 and 5, Table 4). Therefore, the yields decrease with the increase of the molecular size of nitroalkanes as well as of aldehydes. These size-selective behaviours support the assumption that catalysis is promoted by the interior catalytic sites and not only by the exterior ones.

Table 4. Henry reaction of various aldehydes and different nitroalkanes catalyzed by **1**[a]

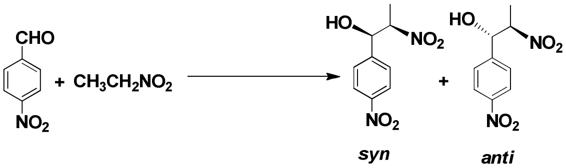


Entry	Aldehyde	Nitroalkane	Yield(%)^{b}
1	 CHO	Nitromethane	91
2	 CHO	Nitroethane	84
3	 CHO	Nitropropane	42
4	 CHO	Nitroethane	45
5	 CHO	Nitroethane	29

[a]Reaction condition: 2.0 mol% of catalyst **1**, aldehyde (1.0 mmol), nitroalkane (0.3 mL) and water (2.0 mL) at 75^{o}C for 40h.

The efficiency of **1** and **2** in comparison with various MOFs that have been used as catalysts in the Henry reaction is shown in Table 5. There are some reports on copper(II) based MOFs[41,71] which are active in the Henry reaction, but the obtained yields are usually lower than those achieved with **1** (entries 1-3, Table 5). Catalyst **2** shows a better or comparable yield with those of other reported zinc MOFs (entries 4-8, Table 5).[42,44,72,73] Moreover, in most of the reported cases, organic solvents have been used for this reaction, and only very few examples are known where water has been applied.[74,75] In our system, interestingly, the reaction yield and the selectivity are higher in aqueous medium than in an organic solvent. The use of an aqueous medium has many advantages owing to the unique properties of water, such as non-toxic, safe and environmentally benign. In that context, our complexes are new, effective, recyclable (see below) and environmentally 'green' catalysts for the Henry reaction.

Table 5. Comparison of activities of MOFs as catalysts for the Henry reaction with 4-nitrobenzaldehyde and nitroethane



Entry	Catalyst	Solvent/Temp/Time	Aldehyde	Yield (%)	Selectivity *syn/anti*	Ref.
1	**1**	Water/75˚C/40h	4-Nitrobenzaldehyde	98	79:21	This work
2	$[Cu_4(HL_{ala})_2(H_2O)_4(MeO)_4]_n$	MeOH/70˚C/24h	4-Nitrobenzaldehyde	95	78:22	41

3	[Cu$_3$(pdtc)(L$_a$)$_2$(H$_2$O)$_3$].2DMF.10H$_2$O	Solvent free/70˚C/36h	4-Nitrobenzaldehyde	78	Not determined	72
4	**2**	Water/75˚C/40h	4-Nitrobenzaldehyde	94	77:23	This work
5	[Zn$_2$(L$_b$)$_2$(4,4'-bipyridine)$_2$(H$_2$O)(DMF)]$_n$	MeOH/70˚C/48h	4-Nitrobenzaldehyde	98	80:20	44
6	[Zn$_3$(TCPB)$_2$·2H$_2$O]· 2H$_2$O·4DMF	Solvent free/70˚C/72h	4-Nitrobenzaldehyde	15	Not determined	72
7	[Zn(3,3'-TPDC)(DABCO)]·DMF·2H$_2$O	Solvent free/60˚C/120h	4-Nitrobenzaldehyde	34	Not determined	73
8	[Zn(L$_c$)(H$_2$O)$_2$]$_n$	MeOH/70˚C/48h	4-Nitrobenzaldehyde	97	80:20	42

HL$_{ala}$ = (2S,2'S,2"S)-2,2',2"-(benzenetricarbonyltris(azanediyl))tripropanoate; L$_a$ = (E)-4-(2-(pyridin-4-yl)vinyl)benzoic acid; L$_b$ = 2-acetamidoterephthalate; TCPB = 1,3,5-tri(4-carboxyphenoxy)benzene; pdtc = pyridine-2,3,5,6-tetracarboxylate; 3,3'-TPDC = terphenyl-3,3,-dicarboxylate; DABCO = 1,4-diazabicyclo[2.2.2]octane; L$_c$ = 5-benzamidoisophthalate.

A possible reaction mechanism for the Henry reaction catalyzed by our MOFs involves the activation of both the aldehyde and nitroethane by the metal centre (with deprotonation of the latter substrate) followed by the formation of C-C bond upon nucleophilic addition of the nitronate to the aldehyde carbonyl group, leading to the β-nitroalkanol.[40-45] The proton abstraction from the nitroalkane ligand and the protonation of the C-C coupled species can be assisted by the ligand (with a carboxylate and an amine group) and also by water (amphoteric behaviour), thus possibly accounting for the good activity of our catalysts in the presence of water. Besides that, in framework **1**, the lability of the DMF ligand and the possible bi- to monodentate carboxylate coordination should lead to coordinative unsaturation, promoting the catalytic activity which also results from the high Lewis basic nature of copper(II).

Typical considerable *syn*/*anti* selectivities of *ca.* 4:1 are obtained (maximum of *ca.* 6:1) for which the rigidity of the L1^{2-} ligand possibly contributes, favoring a parallel type orientation of the coordinated reacting substrates.

Recyclability and Heterogeneity tests

In order to examine the stability of **1** in alcohols oxidation and the Henry reactions, we also tested the recyclability of this heterogeneous catalyst.

For this purpose, we scaled up the nitroaldol reaction for easy separation of catalyst **1** after the reaction. The catalyst was separated upon filtration or centrifugation, washed with methanol and dried at room temperature before being recycled. As shown in Fig. 6, the catalytic system maintained constant reactivity for five consecutive cycles.

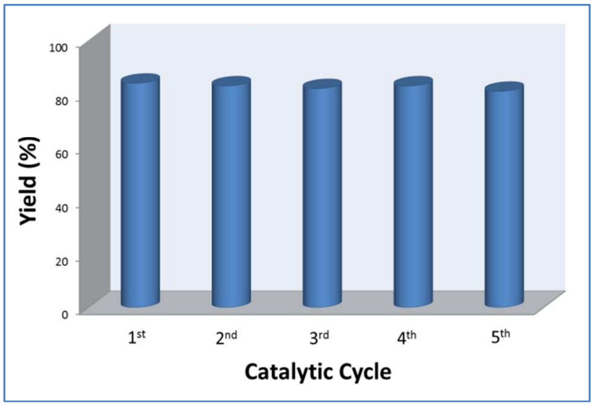


Figure 6 Effect of the catalyst recycling on the yield of β-nitroalkanol from the Henry reaction of benzaldehyde catalyzed by **1**.

In the oxidative media used for the conversion of primary and secondary alcohols to the corresponding aldehydes and ketones, **1** was also able to be reused without loss of activity during 3 consecutive cycles (Figure 7) while maintaining the selectivity. On completion of a stage, the products were analyzed as usually and **1** was recovered by hot filtration from the reaction mixture and dried overnight at 50 º C. The subsequent cycle was initiated upon addition of new standard portions of all other reagents. Moreover, no leaching was detected during the recycling tests: negligible additional yield of products was found up to 1 h reaction after catalyst separation by filtration. This suggests that **1** is a true heterogeneous catalyst, and no catalytically active species were released into solution.

In order to check the structural integrity of the catalyst **1**, in both reactions, we have performed FT-IR and powder X-ray diffraction of catalyst **1** taken before and after the oxidation of alcohols and nitroaldol reactions. They indicate that the structure of the solid was retained (Figure S2).

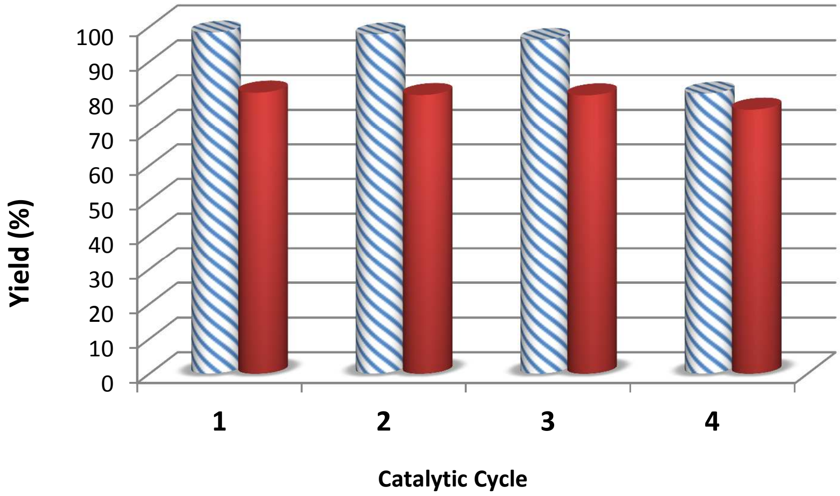


Figure 7 Effect of the catalyst recycling on the yields of acetophenone (-) and benzaldehyde (🟥) from the oxidation of 1-phenylethanol and benzyl alcohol, respectively, catalyzed by **1**.

To further clarify if the catalytic process is heterogeneous or homogeneous, the following test for the nitroaldol reaction was carried out. We performed a controlled experiment with catalyst **1** until an intermediate yield (*ca.* 50%) was observed (6 h), then removed the catalyst by centrifugation and kept the catalyst free reaction solution under the same conditions stirred for additional 35 h. As shown in Fig. 5, after removal of the solid catalyst, the yield of benzaldehyde did not further increase appreciably. These results demonstrate that the catalysis is heterogeneous in nature. Additionally, the filtrated solution, after the separation of the catalyst, was evaporated to dryness and the amount of copper determined was only 0.01% of the amount used in the reaction, thus ruling out any significant leaching of the catalyst.

Conclusion

We successfully isolated three metal organic frameworks (**1** - **3**) of Cu(II), Zn(II) and Cd(II) derived from 5-{(pyridin-4-ylmethyl)amino}isophthalic acid (H_2L1) under different synthetic conditions. Single crystal X-ray diffraction analysis revealed that frameworks **1** and **2** display 2D structures but **3** has a 3D structure. Their construction depends on the particular reaction conditions, which lead to significant differences in the coordination networks. We have also synthesized the salt ($H_3L1^+Cl^-$) of protonated 5-{(pyridin-4-ylmethyl)amino}isophthalic acid and chloride ion and its hydrogen bonding ability. This salt constructs a 2D hydrogen-bonded network via various halogen and hydrogen bonding interactions.

These frameworks (**1** – **3**) exhibit a high activity in an exceptionally short reaction time for the solvent-free MW-assisted oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. These complexes also effectively catalyze the Henry reaction of nitroethane with various aldehydes in aqueous medium producing the corresponding β-nitroalkanols in high yields. Among the three frameworks, compound **1** is the most active one. Therefore, we have synthesized catalysts that are effective in the sequential catalytic conversion of alcohols to aldehydes followed by the conversion of the latter into nitroalkanes. The use of water instead of an organic solvent brings a number of benefits because it is safe, economical, environmentally benign and non-toxic.

We have also proved the stability and recyclability of the catalysts. The copper(II) carboxylate framework **1** can be considered as an heterogeneous 'green' catalyst for the preparation of simple nitro alcohols. It was also demonstrated that the reaction proceeds mainly inside the pore system of compound **1** which is stable under the used conditions.

The above observations provide further evidence that simple MOFs can be utilized as effective heterogeneous catalysts in the important types of reactions of this work. Further studies of the applications of these porous MOFs are in progress.

Supporting Information

Bond distances, angles, and hydrogen bonding tables for all compounds ($H_3L1^+Cl^-$ and **1**-**3**), Crystal Structure Description of $H_3L1^+Cl^-$, FT-IR, and PXRD before and after catalysis, ^1H NMR spectra after the Henry reaction, crystallographic data (CIF).

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Notes

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Reference

(1) Zhou H. –C.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5415-5418.

(2) Zhang, Z.; Zaworotko, M. J. *Chem. Soc. Rev.* **2014**, *43*, 5444-5455.

(3) Zhu, Q. –L.; Xu, Q. *Chem. Soc. Rev.* **2014**, *43*, 5468-5512.

(4) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658.

(5) Elsaidi, S. K.; Mohamed, M. H.; Wojtas, L.; Chanthapally, A.; Pham, T.; Space, B.; Vittal, J. J.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2014**, *136*, 5072–5077.

(6) Karmakar, A.; Goldberg, I. *CrystEngComm* **2011**, *13*, 339-349.

(7) Karmakar, A.; Goldberg, I. *CrystEngComm* **2010**, *12*, 4095-4100.

(8) Karmakar, A.; Oliver, C. L.; *Z. Kristallogr*. **2013**, *228*, 330–334.

(9) Karmakar, A.; Baruah, J. B.; Shankar, R. B. *CrystEngComm* **2009**, *11*, 832-840.

(10) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang L.; Su, C. –Y. *Chem. Soc. Rev.* **2014**, *43*, 6011-6061.

(11) Karmakar, A.; Titi, H. M.; Goldberg, I. *Cryst. Growth Des.* **2011**, *11*, 2621–2636.

(12) Karmakar, A.; Hazra, S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Dalton Trans.* **2015**, *44*, 268-280.

(13) Hu, Z.; Deibert, B. J.; Li, J. *Chem. Soc. Rev.* **2014**, *43*, 5815-5840.

(14) He, Y.; Zhou, W.; Qian, G.; Chen, B. *Chem. Soc. Rev.* **2014**, *43*, 5657-5678.

(15) Kurmoo, M. *Chem. Soc. Rev.* **2009**, *38*, 1353-1379.

(16) Lu, W.; Wei, Z.; Gu, Z. –Y.; Liu, T. –F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle III, T.; Bosch, M.; Zhou, H. –C. *Chem. Soc. Rev.* **2014**, *43*, 5561-5593.

(17) Mulfort, K. L.; Farha, O. K.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 3866–3868.

(18) Farha, O. K.; Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2008**, *47*, 10223–10225.

(19) Karabach, Y. Y.; Kopylovich, M. N.; Mahmudov, K. T.; Pombeiro, A. J. L. *Microwave-assisted catalytic oxidation of alcohols to carbonyl compounds, (ch.18) in: Pombeiro, A. J. L. (Ed.), Advances in Organometallic Chemistry and Catalysis: The Silver/Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book,* Wiley, **2014**, 233–245.

(20) Tojo, G.; Fernandez, M. *Oxidation of Alcohols to Aldehydes and Ketones*, Springer, Berlin, **2006**.

(21) Kopylovich, M. N.; Ribeiro, A. P. C.; Alegria, E. C. B. A.; Martins, N. M. R.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Organomet. Chem*. **2015**, *63*, 91-174.

(22) Sutradhar, M.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Coord. Chem. Rev***.** **2015**, *301-302*, 200-239.

(23) Sutradhar, M.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Alegria, E. C. B. A.; Liu, C. -M.; Pombeiro, A. J. L. *Dalton Trans*. **2014**, *43*, 3966-3977.

(24) Alexandru, M.; Cazacu, M.; Arvinte, A.; Shova, S.; Turta, C.; Simionescu, B. C.; Dobrov, A.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L.; Arion, V. B. *Eur. J. Inorg. Chem.* **2014**, 120-131.

(25) Shul'pin, G. B.; Kirillova, M. V.; Shul'pina, L. S.; Pombeiro, A. J. L.; Karslyan, E. E.; Kozlov, Y. N. *Cat. Commun.* **2013**, *31*, 32–36.

(26) Gryca, I.; Machura, B.; Małecki, J. G.; Shul'pina, L. S.; Pombeiro, A. J. L.; Shul'pin, G. B. *Dalton Trans.* **2014**, *43*, 5759-5776.

(27) Morad, M.; Sankar, M.; Cao, E.; Nowicka, E.; Davies, T. E.; Miedziak, P. J.; Morgan, D. J.; Knight, D. W.; Bethell, D.; Gavriilidis, A.; Hutchings, G. J. *Catal. Sci. Technol.* **2014**, *4*, 3120-3128.

(28) *Microwaves in Organic Synthesis*, *ed.* Loupy, A. Wiley/VCH, Weinheim, **2002**.

(29) *Microwave Assisted Organic Synthesis*, *ed.* Tierney J. P.; Lidström, P. Blackwell Publishing/CRC Press, Oxford, **2005**.

(30) Jlassi, R.; Ribeiro, A. P. C.; Guedes da Silva, M. F. C.; Mahmudov, K. T.; Kopylovich, M. N.; Anisimova, T. B.; Naïli, H.; Tiago, G. A. O.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2014**, 4541–4550.

(31) Ma, Z.; Wei, L.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Dalton Trans.,* **2014**, *43*, 4048-4058.

(32) Nasani, R.; Saha, M.; Mobin, S. M.; Martins, L. M. D. R. S.; Pombeiro, A. J. L.; Kirillov, A. M.; Mukhopadhyay, S. *Dalton Trans***.** **2014**, *43*, 9944-9954.

(33) Timokhin, I.; Pettinari, C.; Marchetti, F.; Pettinari, R.; Condello, F.; Galli, S.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Cryst. Growth Des.* **2015**, *15*, 2303-2317.

(34) Fernandes, R. R.; Lasri, J.; Guedes da Silva, M. F. C.; da Silva, J. A. L.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *J. Mol. Catal. A Chem.* **2011**, *351*, 100–111.

(35) Shixaliyev, N. Q.; Gurbanov, A. V.; Maharramov, A. M.; Mahmudov, K. T.; Kopylovich, M. N.; Martins, L. M. D. R. S.; Nenajdenko, V. G.; Pombeiro, A. J. L. *New J. Chem.* **2014**, *38*, 4807-4815.

(36) Li, L.; Matsuda, R.; Tanaka, I.; Sato, H.; Kanoo, P.; Jeon, H. J.; Foo, M. L.; Wakamiya, A.; Murata, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2014**, *136*, 7543−7546.

(37) Shibasaki, M.; Kanai, M.; Matsunaga, S.; Kumagai, N. *Multimetallic Multifunctional Catalysts for Asymmetric Reactions: Bifunctional Molecular Catalysis* (*ed*. Ikariya, T.; Shibasaki, M.), *Topics in Organometallic Chemistry, Springer-Verlag Berlin Heidelberg,* **2011**, *37*, 1-30.

(38) Milner, S. E.; Moody, T. S.; Maguire, A. R. *Eur. J. Org. Chem.* **2012**, 3059–3067.

(39) Luzzio, F. A. *Tetrahedron* **2001**, *57*, 915-945.

(40) Karmakar, A.; Hazra, S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *New J. Chem.* **2014**, *38*, 4837-4846.

(41) Karmakar, A.; Oliver, C. L.; Roy, S.; Öhrström, L. *Dalton Trans.* **2015**, *44*, 10156-10165.

(42) Karmakar, A.; Guedes da Silva, M. F. C.; Hazra, S.; Pombeiro, A. J. L. *New J. Chem.* **2015**, *39*, 3004-3014.

(43) Hazra, S.; Karmakar, A.; Guedes da Silva, M. F. C.; Dlháň, Ľ.; Boča, R.; Pombeiro, A. J. L. *New J. Chem.* **2015**, *39*, 3424-3434.

(44) Karmakar, A.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Dalton Trans.* **2014**, *43***,** 7795–7810.

(45) Rocha, B. G. M.; Mac Leod, T. C. O.; Guedes da Silva, M. F. C.; Luzyanin, K. V.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Dalton Trans.* **2014**, *43*, 15192-15200.

(46) Chen, M. –S.; Bai, Z. –S.; Okamura, T.; Su, Z.; Chen, S. –S.; Sun, W. –Y.; Ueyama, N. *CrystEngComm* **2010**, *12*, 1935-1944.

(47) Chen, M. –S.; Su, Z.; Chen, M.; Chen, S. –S.; Li, Y. –Z.; Sun, W. –Y. *CrystEngComm* **2010**, *12*, 3267-3276.

(48) Das, M. C.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2009**, *131*, 10942–10949.

(49) Das, M. C.; Bharadwaj, P. K. *Chem. Eur. J.* **2010**, *16*, 5070–5077.

(50) Chen, M. –S.; Chen, M.; Takamizawa, S.; Okamura, T.; Fan J.; Sun, W. –Y. *Chem. Commun.* **2011**, *47*, 3787-3789.

(51) Bulbule, V. J.; Deshpande, V. H.; Velu, S.; Sudalai, A.; Sivasankar, S.; Sathe, V. T. *Tetrahedron* **1999**, *55*, 9325-9332.

(52) Bruker, *APEX2 & SAINT, AXS Inc.*, Madison, WI, **2004**.

(53) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

(54) Farrugia, L. J. *J. Appl. Crystallogr*. **1999***, 32*, 837-838.

(55) Spek, A. L. *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

(56) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 5th edn, Wiley & Sons, New York, **1997**.

(57) Munoz-Hernandez, M. -A.; Keizer, T. S.; Wei, P.; Parkin, S.; Atwood, D. A. *Inorg. Chem.* **2001**, *40*, 6782–6787.

(58) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.

(59) Blatov, V. A. *Struct. Chem.* **2012***, 23,* 955-963.

(60) Mattalia, J. M.; Vacher, B.; Samat, A.; Chanon*,* M. *J. Am. Chem. Soc.* **1992**, *114*, 4111-4119.

(61) Dronova, M. S.; Bilyachenko, A. N.; Yalymov, A. I.; Kozlov, Y. N.; Shul’pina, L. S.; Korlyukov, A. A.; Arkhipov, D. E.; Levitsky, M. M.; Shubina, E. S.; Shul’pin, G. B. *Dalton Trans.* **2014**, *43*, 872-882.

(62) Kirillova, M. V.; Kuznetsov, M. L.; Kozlov, Y. N.; Shul’pina, L. S.; Kitaygorodskiy, A.; Pombeiro, A. J. L.; Shul’pin, G. B. *ACS Catal.* **2011**, *1*, 1511–1520.

(63) Fei, H.; Shin, J. W.; Meng, Y. S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S. M. *J. Am. Chem. Soc.* **2014**, *136*, 4965−4973.

(64) Paul, M.; Adarsh, N. N.; Dastidar, P. *Cryst. Growth Des*. **2014**, *14*, 1331−1337.

(65) Zhang, X.; Dong, W.; Luan, Y.; Yang, M.; Tan, L.; Guo, Y.; Gao, H.; Tang, Y.; Dang, R.; Li, J.; Wang, G. *J. Mater. Chem. A* **2015**, *3*, 4266–4273.

(66) Zhu, J.; Wang, P. C.; Lu, M. *Appl. Catal. A: Gen.* **2014**, *477*, 125-131.

(67) Qi, Y.; Luan, Y.; Yu, J.; Peng, X.; Wang, G. *Chem. Eur. J.* **2015**, *21*, 1589–1597.

(68) Peng, L.; Zhang, J.; Xue Z.; Han, B.; Sang, X.; Liu, C.; Yang, G. *Nat. Commun*. **2014**, 5:4465.

(69) Paul, M.; Adarsh, N.N.; Dastidar P. *Cryst. Growth Des*. **2014**, *14*, 1331-1337.

(70) Feng X.; Xu, C.; Wang, Z. -Q.; Tang, S-F.; Fu, W. -J.; Ji, B-M.; Wang, L. -Y. *Inorg. Chem.* **2015**, *54*, 2088-2090.

(71) Shi, L. –X.; Wu, C. –D. *Chem. Commun.* **2011**, *47*, 2928-2930.

(72) Lin, X. -M.; Li, T. -T.; Wang, Y. -W.; Zhang, L.; Su, C. -Y. *Chem. Asian J.* **2012**, *7*, 2796-2804.

(73) Gu, J. –M.; Kim, W. –S.; Huh, S. *Dalton Trans.* **2011**, *40*, 10826-10829.

(74) Chintala, P.; Ghosh, S. K.; Long, E.; Headley, A. D.; Nia, B. *Adv. Synth. Catal.* **2011**, *353*, 2905-2909.

(75) Lai, G.; Guo, F.; Zheng, Y.; Fang, Y.; Song, H.; Xu, K.; Wang, S.; Zha, Z.; Wang, Z. *Chem. Eur. J.* **2011**, *17*, 1114-1117.

Table of Contents

Metal–Organic Frameworks with Pyridyl-Based Isophthalic Acid and Their Catalytic Applications in Microwave Assisted Peroxidative Oxidation of Alcohols and Henry Reaction

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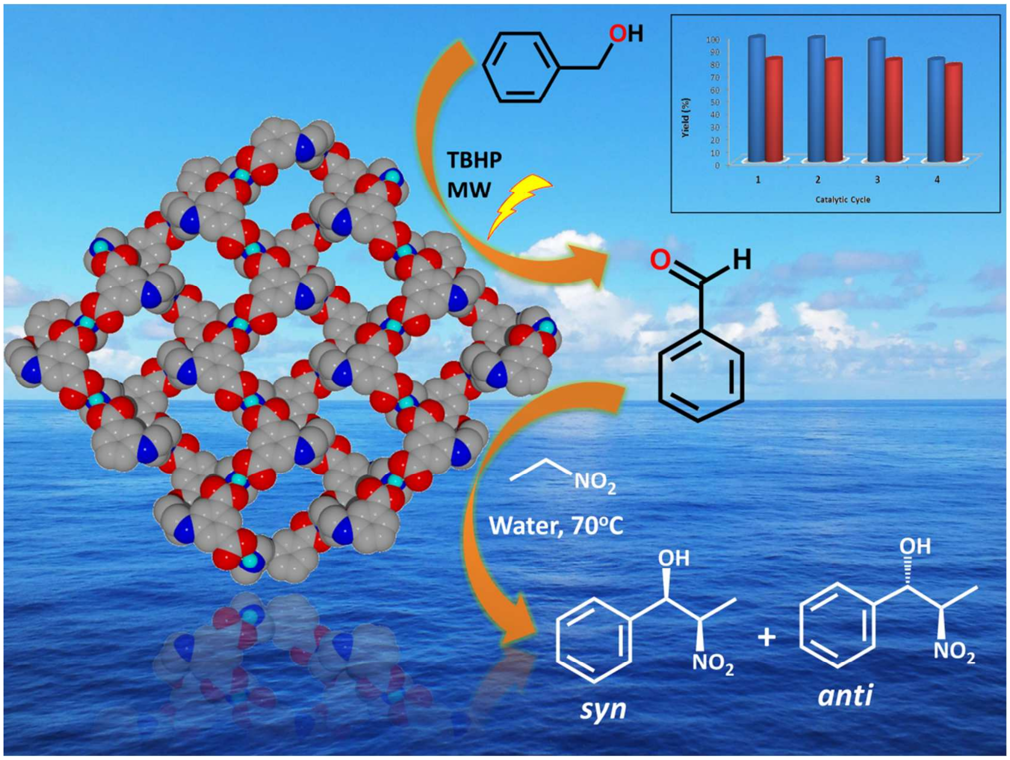

Synopsis

5-{(pyridin-4-ylmethyl)amino} isophthalic acid is used to synthesize three new copper(II), zinc(II) and cadmium(II) MOFs which act as heterogeneous catalysts for the peroxidative oxidation of alcohols as well as for the Henry reaction of different aldehydes in water.