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Amide Functionalized Metal Organic Frameworks for Diastereoselective Nitroaldol (Henry) Reaction in Aqueous Medium

Anup Paul,[a]* Anirban Karmakar,[a] M. Fátima C. Guedes da Silva,[a]* Armando J. L. Pombeiro[a]*

[a]*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa. Portugal. E-mail:* *kanupual@gmail.com*, *fatima.guedes@tecnico.ulisboa.pt*, *pombeiro@tecnico.ulisboa.pt*

Abstract

The two new metal-organic frameworks (MOFs) of zinc(II) and copper(II) $[Zn_2L_2(1,4\text{-}BDC)]_n\cdot 2n(DMF)$ (**1**) and $[Cu(L)_2]_n.4n(DMF).n(H_2O)$ (**2**) (L = 4-(pyridin-4-ylcarbamoyl)benzoate; BDC = benzenedicarboxylate), respectively, have been synthesized from a pyridyl amide functionalized benzoic acid (**HL**). They were characterized by elemental, FT-IR, thermogravimetric, powder X-ray and single crystal X-ray diffraction analyses. Single crystal X-ray crystallography reveals that **1** and **2** exhibit 2D and 3D polymeric architectures, respectively. Topological analysis illustrate a 6-connected pcu alpha-Po primitive cubic for **1** and a 8-connected body centred cubic (bcu) topology for **2**. Both **1** and **2** act as heterogeneous catalysts for the nitroaldol reaction in aqueous medium, with a high yield and moderate to good diastereoselectivities under ambient conditions. They can be recycled and reused without any significant loss of the catalytic efficiency.

Introduction

The design and construction of metal-organic frameworks (MOFs)[1], also known as coordination polymers (CPs), have attracted enormous attention owing, *e.g.*, to their simplistic preparation, structural diversity, tunable pore metrics and easy functionalization of their surfaces. As a result, MOFs have found widespread applications in storage of fuel and environmental gases,[2,3] molecular separation,[4] luminescence,[5] magnetism,[6] drug delivery,[7] biomedical imaging[8] and sensing.[9] Recently, MOFs have found applications in the field of catalysis,[10-15] where their high density of active sites and high porosity can be advantageous features. Usually, the catalytic activity of MOFs is dependent, *e.g.*, on the Lewis acidity of the metal cations,[12] the presence of basic groups[13,14] (such as pyridine, amide and amine) in constructing linkers and the redox properties of the metal centres.[10,11,15]

Thus, in pursuing our interest on the synthesis of MOFs for possible application in catalysis,[10-14] we chose 4-(pyridin-4-ylcarbamoyl)benzoic acid (**HL**) as a ligand source (Fig. 1), based on the following reasons: (i) the amide backbone in the ligand framework may provide a basic environment which may facilitate the catalytic reaction[13*b*,16]; (ii) the ligand comprises multiple coordinating groups which should be suitable for building extended frameworks with a large surface area, also favourable for catalysis.

Concerning a possible catalytic application, the nitroaldol (or Henry) reaction is as an important carbon-carbon bond formation reaction and widely used in organic synthesis.[11,17-20] The resulting *α*-hydroxy nitro compounds are valuable starting materials for, *e.g.*, 1,2-amino alcohols or β-hydroxy acids.[21] Generally, such a reaction is performed with homogeneous basic catalysts, such as alkali metal hydroxides, alkoxides or amines, with a good efficiency.[22] A number of homogeneous catalysts have already been reported by our group for such a type of reaction.[10*a*,11,23]

However, heterogeneous catalysts for such a transformation are scant,[10*a*,11*d-g*,24-28] and thus we wish to extend this topic. On the other hand, organic reactions in water have attracted a significant attention because of the natural abundance and non-toxicity of this medium as compared to typical organic solvents.[29,30] Recently, a few mononuclear copper(II) complexes were reported by our group[11*d*] to act as heterogeneous catalysts in water towards the nitroaldol reaction, but the obtained yield (77%) should be improved. Thus, the development of new, efficient and selective heterogeneous catalysts in aqueous medium would be a significant addition to this field and are worth exploring. Further, to our knowledge there are no reports on Zn(II) or Cu(II) MOF catalysts, where the Henry reaction has been performed in aqueous medium.

Hence, in quest for developing efficient heterogeneous catalysts for the Henry reaction in aqueous medium, herein we present the syntheses and crystal structures of two new MOFs with a bridged amide pyridyl benzoate (**L**$^-$, Fig. 1), *viz.* [Zn_2L_2(1,4-BDC)]$_n$·2n(DMF) (**1**) (BDC = benzenedicarboxylate) and [$Cu(L)_2$]$_n$.4n(DMF).n(H_2O) (**2**), and their catalytic application in such a reaction. The structural features of the obtained MOFs have been established by single crystal X-ray diffraction, topological and thermogravimetric studies.

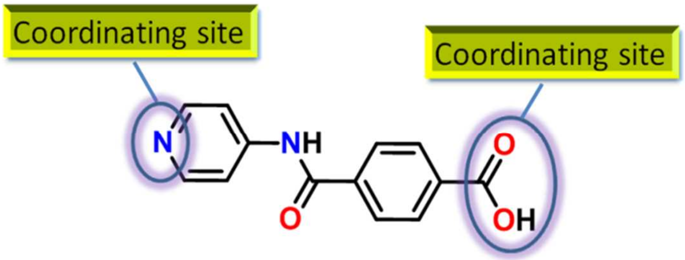


Fig. 1. 4-(pyridin-4-ylcarbamoyl)benzoic acid (**HL**).

Experimental Section

Materials and Physical Measurements

Solvents were dried and distilled prior to their use following standard procedures.[31] 4-aminopyridine, terephthalic acid (H_2DA), thionyl chloride ($SOCl_2$) and the metal nitrates $Zn(NO)_3.6H_2O$ (98.0% purity) and $Cu(NO_3)_2.3H_2O$ were purchased from Sigma Aldrich Chemical Co. and used as received. Methyl-4-(chlorocarbonyl)benzoate was prepared following established literature procedures with slight modifications.[32] FT-IR spectra were recorded on a Bruker Vertex 70 instrument in KBr pellets. ^1H (300 MHz) and ^{13}C (75.45 MHz) NMR spectra were obtained at room temperature (RT) on a Bruker Avance II + 300 (UltraShield^{TM}Magnet) spectrometer using tetramethylsilane [$Si(CH_3)_4$] as an internal reference. Carbon, hydrogen and nitrogen elemental analyses were carried out by 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-2-theta 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°.

Synthesis of 4-(pyridin-4-ylcarbamoyl)benzoic acid (HL)

The synthesis of the ligand (**HL**) involves a five-step reaction sequence. The first three-steps concern, the synthesis of monomethyl ester chloride from terephthalic acid, used in the synthesis of the **HL**, and are described in the experimental Section of supporting information (ESI). The relevant ^1H and ^{13}C NMR spectra are presented in Figs. S1-S6, ESI.

In the fourth step, a solution of 4-aminopyridine (0.5 g, 5.3 mmol) and distilled triethylamine (3.0 mL, 28 mmol) in anhydrous THF (100 mL) was added dropwise to a solution of methyl 4-(chlorocarbonyl)benzoate (1 g, 5 mmol) in anhydrous THF (100 mL) at room temperature.

Triethylamine (3.0 mL, 28 mmol) was added, and the reaction mixture was stirred for 24 h. The resulting white product of methyl 4-(pyridin-4-ylcarbamoyl)benzoate thus formed was collected by filtration, washed with THF and several times with water, and dried under vacuum to get the desired methyl ester **MeL** (1.2 g, 80%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm,): δ 10.79 (s, 1H, NH), 8.50 (d, 2H, J = 6.3 Hz, H_{py}), 8.10 (d, 2H, J = 9.0 Hz, H_{Ar}), 8.07 (d, 2H, J = 9.0 Hz, H_{py}), 7.79 (d, 2H, J = 6.0 Hz, H_{Ar}), 3.90 (s, 3H, -O-CH_3). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ ppm): 167.94, 165.62, 136.12, 135.20, 133.86, 132.56, 131.46, 129.40, 52.78 (-O-CH_3) ESI-MS : m/z $[(M + H)]^+$, Calcd. 243.23, found 243.1.

Finally, the isolated **MeL** (1 g, 4 mmol) and NaOH (0.5 g, 13 mmol) were dissolved in 20 mL of MeOH:H_2O (4 : 1). The resultant reaction mixture was refluxed for 6 h at 80 °C, after which the solvent was reduced nearly to dryness under reduced pressure and the solution was acidified (pH~ 1-2) with dilute HCl solution. The white solid product of **HL** thus obtained was removed by filtration, washed several times with water until neutral and dried under vacuum (yield: 0.6 g, 60%). Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.72; H, 4.32; N, 11.43. FT-IR (KBr, cm^{-1}): 3383 (bs), 2547 (mb), 1691 (s), 1590 (s), 1507 (s), 1378 (s), 1320 (m), 1196 (m), 1109 (w), 1057 (w), 961 (s), 759 (s), 883 (s), 730 (s), 528 (w); ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): δ 10.80 (s, 1H, NH), 8.52 (d, 2H, J = 6.0 Hz, H_{py}), 8.10 (d, 2H, J = 6.0 Hz, H_{Ar}), 8.04 (d, 2H, J = 9.0 Hz, H_{py}), 7.83 (d, 2H, J = 6.0 Hz, H_{Ar}). ^{13}C-NMR (77 MHz, DMSO-d_6, δ ppm): 167.15, 166.14, 160.50, 150.58, 146.20, 137.91, 137.21, 134.30, 129.93, 128.62. ESI-MS : m/z $[(M + H)]^+$, Calcd. 243.07, found 243.1, $[(M + Na)]^+$, Calcd. 265.07, found 265.1.

Synthesis of $[Zn_2(L)_2(1,4\text{-BDC})]_n.2n(DMF)$ (1)

$Zn(NO_3)_2.6H_2O$ (6.6 mg, 0.022 mmol), **HL** (5 mg, 0.022 mmol) and terephthalic acid (5 mg, 0.022 mmol) were placed in H_2O (1 mL) and DMF (1 mL) in a sealed 8 mL glass vessel and heated at 80˚C for 48 h. White crystals of **1** were obtained upon gradual cooling to room temperature (at 0.2 ˚C min^{-1}), washed with deionized water, DMF and then dried in air. **1** is not soluble in the usual solvents. Yield: 70% (based on Zn). Anal. Calcd for $C_{40}H_{36}N_6O_{12}Zn_2$: C, 52.01; H, 3.93; N, 9.10. Found: C, 51.99; H, 3.91; N, 9.06. IR (KBr/pellet, cm^{-1}): 3080 (w, br), 1666 (w), 1596 (s), 1516 (w), 1428 (s), 1388 (s), 1331 (w), 1296 (m, sh), 1210 (m), 1095 (w), 1024 (m), 897 (m), 841 (m), 732 (s, br), 573 (m), 538 (m).

Synthesis of $[Cu(L)_2]_n.4n(DMF).n(H_2O)$ (2)

A similar synthetic procedure as that used for **1** was followed, but using **HL** (15 mg, 0.067 mmol) and $Cu(NO_3)_2.3H_2O$ (10 mg, 0.060 mmol) in DMF: H_2O (1 mL:1 mL), without terephthalic acid. The blue block crystals of **2** suitable for X-ray diffraction analysis obtained were subsequently washed with water, DMF and dried in air. **2** is not soluble in the usual solvents. Yield: 60% (based on Cu). Anal. Calcd for $C_{41}H_{54}CuN_9O_{11.5}$ [obtained from a batch different of that used for X-ray analysis and fitting to $[Cu(L)_2]_n.5n(DMF).0.5n(H_2O)$]: C, 53.97; H, 5.97; N, 13.81. Found: C, 53.93; H, 5.92; N, 13.78. IR (KBr/pellet, cm^{-1}): 3426 (w, br), 1678 (w), 1595 (w), 1518 (w), 1386 (s), 1334 (w), 1297 (m), 1267 (m), 1213 (s), 1099 (w), 1026 (m), 875 (m), 836 (m), 732 (s, br), 538 (m), 471 (m).

Procedure for nitroaldol (Henry) reaction catalyzed by the MOFs 1 and 2

In a typical reaction, a mixture of an aldehyde (1 mmol), nitroethane (4 mmol) and the Zn- or the Cu-MOF catalyst (3.0 mol %) was placed in a capped glass vessel, and then 2.0 mL water was added into it. The mixture was heated at 70 °C for 48 h, and subsequently quenched by centrifugation and filtration at room temperature. The filtrate was extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulfate; subsequent evaporation of the solvent gave the crude product. The product was dissolved in $CDCl_3$ and analyzed using ^{1}H NMR. The yield of the β-nitroalkanol product (relative to the aldehyde) was established typically by taking into consideration the relative amounts of these compounds, as given by ^{1}H NMR and as previously reported.[11*d-g*] The ratio between the *syn* and *anti* isomers was also determined by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra, the values of vicinal coupling constants (for the β-nitroalkanol products) between the α-N–C–H and the α-O–C–H protons identify the isomers, being J = 7-9 or 3.2-4 Hz for the *syn* or *anti* isomers, respectively.[11*d-g*] The yield and selectivity of MOFs **1** and **2** for the Henry reaction was calculated (see Figs. S12-S13, ESI, as examples) according to a procedure reported earlier on the basis of ^{1}H-NMR spectra.[11*e*]

The catalytic recycling experiment was performed by washing the used catalyst (separated by centrifugation and filtration of the supernatant solution) with water and dried in air at room temperature. It was then subsequently reused for the nitro-aldol (Henry) reaction as described above.

Crystal Structure Determination

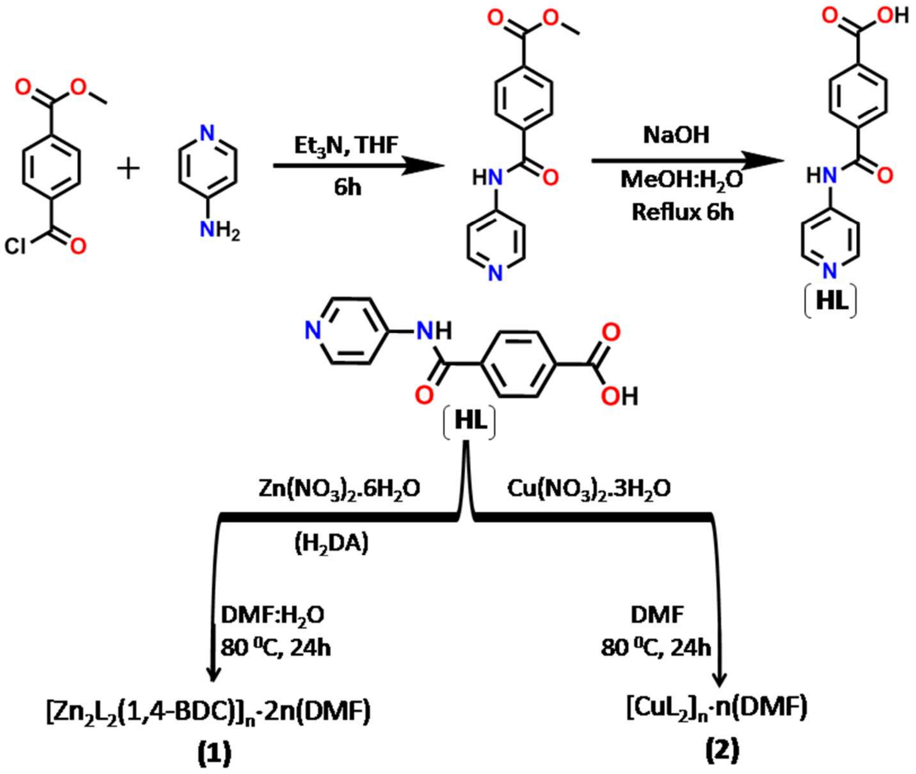
X-ray quality single crystals of the compounds were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature (**1**) or at 150 K (**2**). Intensity data were collected using a Bruker AXS-KAPPA APEX II or a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71069) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using

Bruker SMART[33a] software and refined using Bruker SAINT[33a] on all the observed reflections. Absorption corrections were applied using SADABS.[33a] Structures were solved by direct methods by using SIR97[33b] and refined with SHELXL-2014/7.[33c] Calculations were performed using the WinGX System-Version 2014.1,[33d] and molecular graphics were done with Mercury 3.5.1.[33e] The hydrogen atoms attached to carbon 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 carbon atoms for phenyl and methylene residues and 1.5Ueq for methyl groups. The hydrogen atoms bound to nitrogen were located from the final difference Fourier map and their positions refined with DFIX restraints, and with Uiso = 1.5Ueq of their parent N-atoms. For the final refinements of structure **1**, the TWIN/BASF instructions were included in the SHELXL2014 instruction file, in order to take into consideration the contribution of two twin components to the structure-factor calculations during the least-squares optimization; the major twin fraction refined to 0.499 (15). The Platon SQUEEZE procedure[33e] was applied to compound **2** to recover 538 electrons per unit cell in a void (total volume 1445 Å^3), that is, 135 electrons per formula unit. The electron count suggests the presence of *ca*. one water and three dimethylformamide molecules per asymmetric unit. These were removed from the crystal structures, but included in the empirical formula of CIF. The thermogravimetric analysis and the elemental analysis also support these results. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. Crystallographic data are summarized in Table 1 and selected bond distances and angles are presented in Tables S1 and S2, ESI. CCDC 1414611 and 1414612 for **1** and **2**, respectively, 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

Synthesis and Characterization

The ligand 4-(pyridin-4-ylcarbamoyl)benzoic acid **(HL)** was synthesised (Scheme 1) by reacting 4-aminopyridine with methyl 4-(chlorocarbonyl)benzoate in anhydrous THF in the presence of triethyamine, followed by hydrolysis according to a literature procedure.[11g] It was characterized by elemental, IR, ^{1}H and ^{13}C NMR and ESI-MS analyses. The ^{1}H and ^{13}C NMR spectra are presented in Figs. S7-S10, ESI. Compounds **1** and **2** were synthesized (Scheme 1) by hydrothermal reaction of **HL** with $Zn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$, respectively, in the former case in the presence of terephthalic acid (H_2DA), and were characterized by elemental analysis, IR, single crystal X-ray crystallography, powder X-ray diffraction and thermogravimetric analyses (Fig. S11, ESI). They are insoluble in water and in common organic solvents.



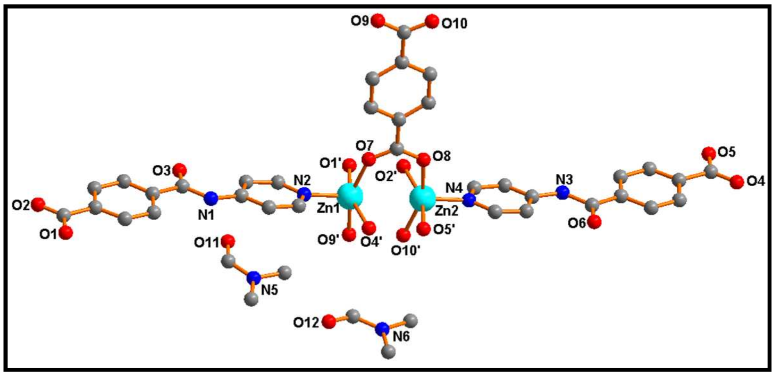
Scheme 1. Syntheses of **HL**, zinc(II) (**1**) and copper(II) (**2**) MOFs.

Their infrared spectra (Fig. S12, ESI) support the metal coordination of the carboxylate group of **L**$^-$. The band due to the asymmetric stretching vibration [υ_{asym}(OCO)] exhibits a shift of *ca.* 100 cm^{-1} relative to the free ligand **HL** (1691 cm^{-1}), being observed at 1596 cm^{-1} and 1595 cm^{-1} for **1** and **2,** respectively. The coordination of the carboxylate group is confirmed by X-ray crystal structure determination as discussed below.

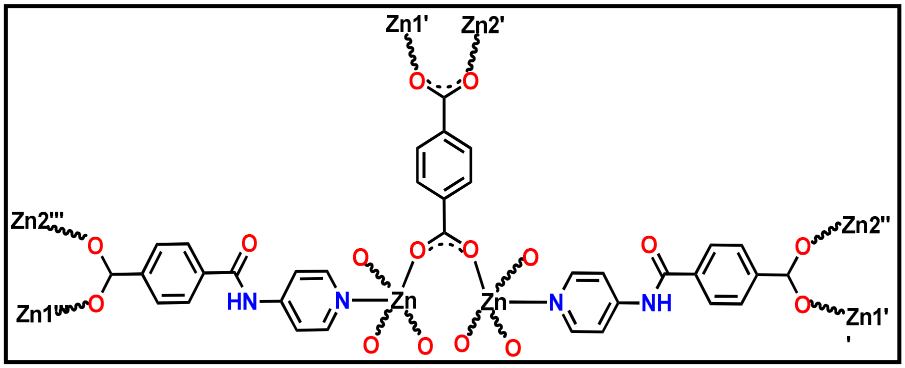
Crystal structure analysis

Single-crystal X-ray diffraction studies of **1** revealed that it crystallizes in the monoclinic P2$_1$ space group, and that the asymmetric unit contains two Zn^{2+} ions, two deprotonated ligands L$^-$, one benzenedicarboxylate and two non-coordinated DMF molecules [Figs. 2(A) and 2(B)]. The L$^-$ and 1,4-benzenedicarboxylate ligands coordinate to the metal centres in a bridging bidentate fashion, the former remaining almost planar as indicated by the angle between the least square planes of the phenyl and of the piridyl rings (*ca.* 10.13 º). Compound **1** features a rhombic grid type three-dimensional framework having approximately 11 x 15 Å^2 channels along the crystallographic *b*-axis [Fig. 2(C)] and with 3-fold interpenetrating networks [Fig. 4(C)]. The dinuclear zinc(II) paddle-wheel clusters act as secondary building blocks through four L$^-$ and two 1,4-benzenedicarboxylate ligands. Both the Zn(II) centres adopt square pyramidal geometries (τ_5 of 0.00).[34] The equatorial planes of the metal ions are occupied by four O-atoms, two from L$^-$ and other two from 1,4-benzenedicarboxylate ligands; the axial site is engaged with the pyridyl N-atom. The Zn-O bond lengths are in the range of 2.019(3)-2.084(4) Å and the Zn-

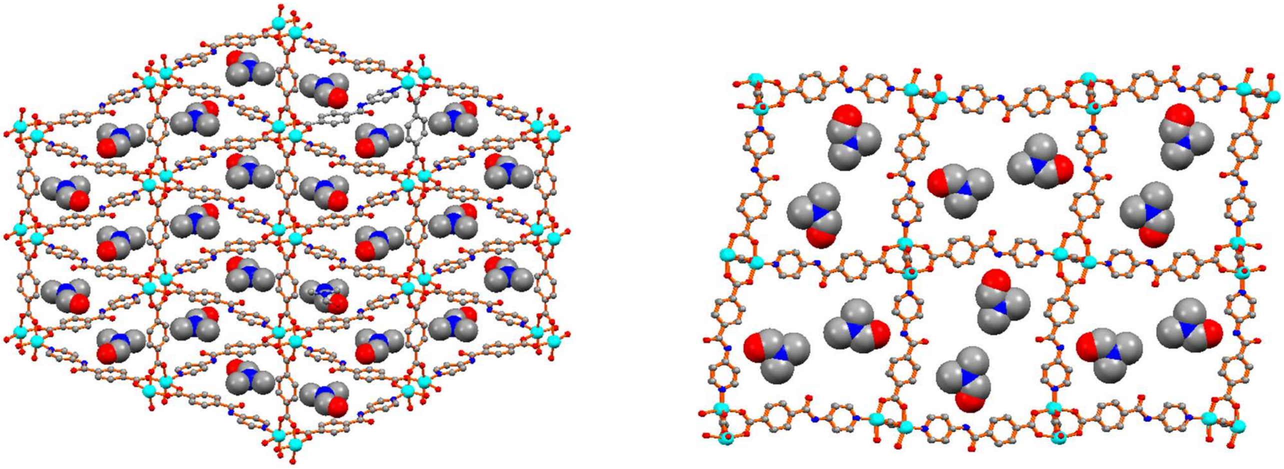
N distances lie between 2.010(5) and 2.025(4)Å. The shortest metal···metal distance in **1** is of 2.9936(5) Å**.**



(A)



(B)

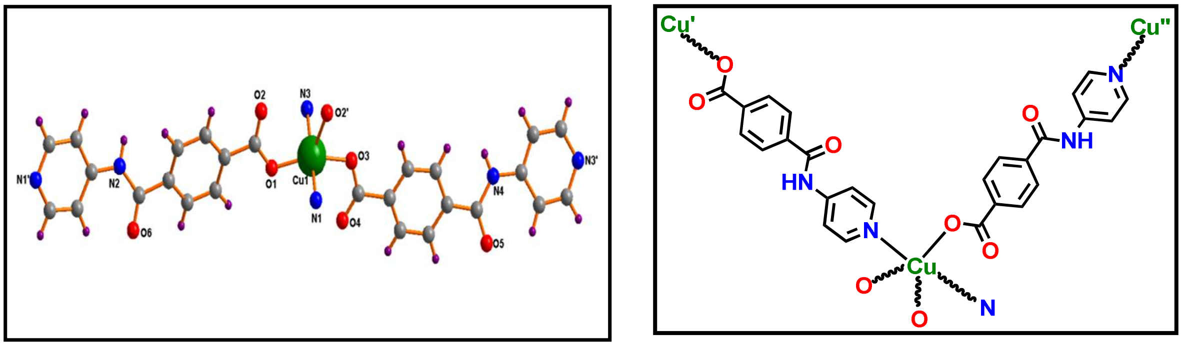


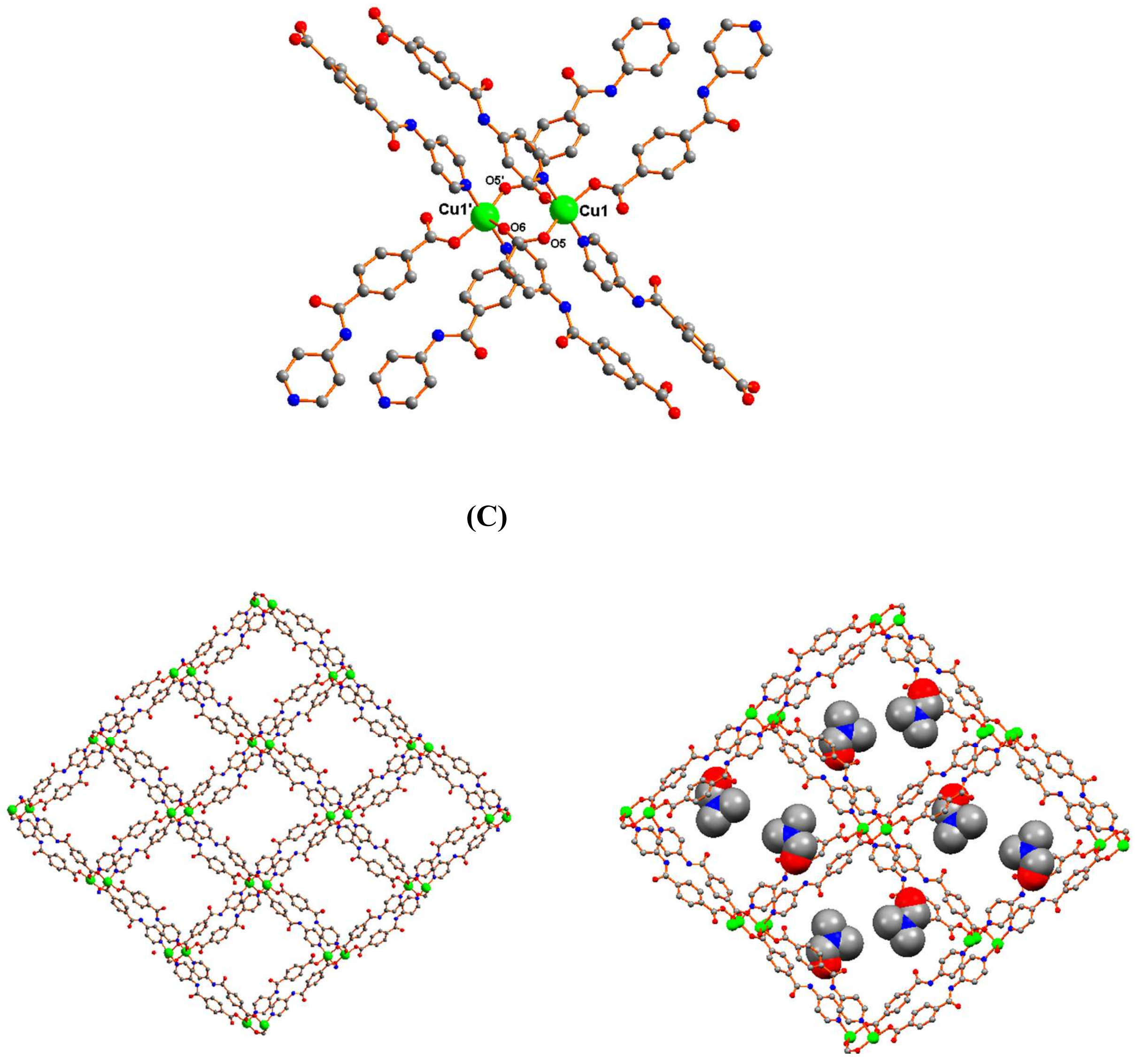
(C) (D)

Fig. 2. (A) Asymmetric unit of **1** with partial atom labelling scheme; (B) Schematic representation of an asymmetric unit of **1** (excluding DMF molecules); representation of the 3D network of **1** along the crystallographic *a*-axis (C) and *b*-axis (D) (DMF molecules are represented as spacefill model. Hydrogen atoms are omitted for clarity.

The DMF molecules are encapsulated in the lattice [Fig. 2(D)] and involved in hydrogen bonding interactions connecting the amide NH- moiety as donor and the oxygen from DMF as acceptor [N4-H4N···O20, D···A 2.985(8)Å, <DHA 157(5)°; N6-H6N···O21, D···A 2.980(9)Å, <DHA 164(5)°]. Several C-H···O interactions are also relevant and help to stabilize the lattice (Table S2, ESI).

Compound $[Cu(L)_2]_n.4n(DMF).n(H_2O)$ (2) crystallizes in the monoclinic $P2_1/n$ space group, its asymmetric unit containing one Cu^{2+} ion, two deprotonated L^- ligands and one non-coordinated DMF molecule [Figs. 3(A) and (B)]. The dimetallic cluster in **2** acts as a secondary building block through eight L^- ligands [Fig. 3(C)]. The Cu(II) centre presents a distorted square pyramidal geometry (τ_5= 0.32),[35] the equatorial plane including two O-atoms and two N-atoms, whereas the axial site is occupied by one carboxylate O-atom. The Cu-O bond lengths are in the 1.961(3)-2.342(4) Å range and the Cu-N distances assume values of 2.004(4) and 2.020(4) Å. The minimum metal···metal distance is of 4.340(1) Å.





(A) **(B)**

(C)

(D) **(E)**

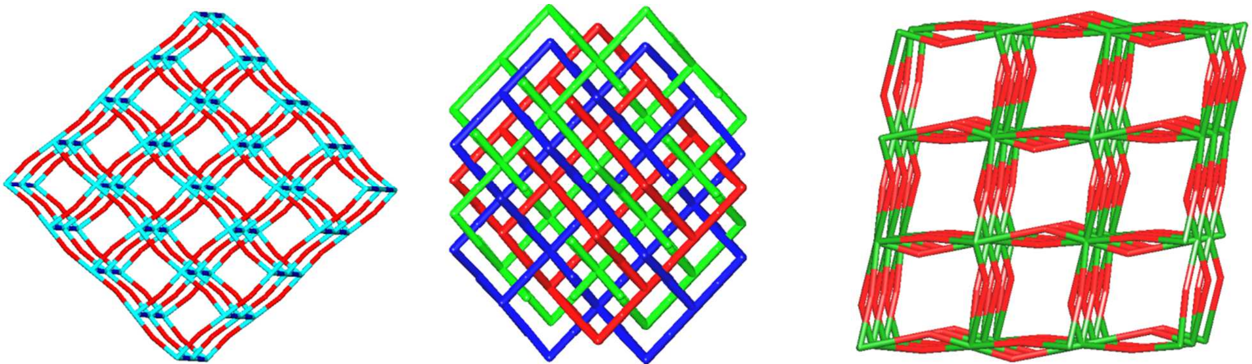
Fig. 3. (A) Asymmetric unit of **2** with partial atom labelling scheme; (B) Schematic representation of the asymmetric unit of **2** (excluding DMF molecules); (C) representation of the

3D network of **2**; (D) 3D packing diagram of **2**; (E) 3D packing diagram of **2** (DMF molecules are represented as space fill model). Hydrogen atoms are omitted for clarity.

The packing view of **2** is characterized by open channels along the crystallographic *a*-axis [Fig. 3(D)] with approximate dimension of 15 x 15 Å^2 and a void space of 34% per unit cell according to PLATON.[33e] The open channels are occupied by DMF molecules which are hydrogen bonded through the amide hydrogen atoms to the network [N2–H2N···O8, D···A 2.943(6)Å, <DHA 171(4)°] [Fig. 3(E)]. Intermolecular C-H···O contacts are relevant and help to stabilize the structure (Table S2, ESI).

Topological analysis

To improve the description of the crystal structures of **1** and **2** their topological analysis was performed[36] by reducing their multidimensional structures to simple node-and-linker nets where the metallic nodes and the organic linkers represent secondary building units (SBUs).[36*a,b*] The entire lattice and coordinated solvent molecules were first removed from the frameworks. In case of **1**, the dinuclear zinc(II) unit was considered as a single node coordinated to two L and four 1,4-benzenedicarboxylate anions, thus affording a 6-connected pcu alpha-Po primitive cubic topology [Fig. 4(A)]. This network also has threefold interpenetrated nets as presented in Fig. 4 (B). In case of **2,** where each Cu1 centre is coordinated to four different carboxylate ligands, the dinuclear unit was considered as a single node which subsequently coordinated *via* 8 different carboxylate linkers. As a result, the framework represents an 8-connected body centred cubic (bcu) topology [Fig. 4(C)].



(A) (B) (C)

Fig. 4. Node-and-linker-type descriptions of the 2D coordination frameworks in **1** (A), of the 3D coordination frameworks in **2** (B), and the three fold interpenetrated network of **1** (C).The metal nodes are represented in green (Cu) and cyan (Zn) and the linkers in red.

Catalytic activity of MOFs 1 and 2 for the nitro-aldol reaction

In view of the insolubility of the frameworks **1** and **2** in water, we have tested them as solid heterogeneous catalysts for the nitroaldol (or Henry) reaction in water of nitroethane with various aldehydes (Scheme 2). In a typical reaction, a mixture of aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and **1** or **2** (3.0 mol %) in 2.0 mL water, contained in a capped glass vessel, was stirred at 70˚C for 48 h, whereupon the solution was filtered or centrifuged to remove the solid catalyst. The filtrate was extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulfate; subsequent evaporation of the solvent gave the crude product which was a mixture of the β-nitroalkanol diastereoisomers (*syn* and *anti* forms, with predominance of the former; Scheme 2) which were analyzed by ^{1}H NMR (Figs. S13-S14, ESI).

To begin with, MOFs **1** and **2** were screened as catalysts with *p*-nitrobenzaldehyde and nitroethane as representative substrates; we found that **1** showed a slightly higher catalytic activity than **2** under similar experimental conditions. This eventually could be accounted for by the higher Lewis acidic nature of Zn(II). Hence, the optimization of the reaction conditions with reaction time (2-60 h), catalyst loading (1-7 mol %) and temperature (22-80 °C) was investigated in a model *p*-nitrobenzaldehyde and nitroethane system with **1** as catalyst (Table 2).

When 3 mol% of solid compound **1** was used as catalyst at 70˚C, an yield of 93% (*syn*/*anti* = 74:26) of benzaldehyde into β-nitroalkanol is reached (entry 1, Table 2) after 48 h, which does not change upon further prolongation of the reaction time to 60 h (entry 24, Table 2) [Fig. 5(A)]. With **2** as catalyst a slightly lower yield of 90% (*syn*/*anti* = 65:35) was obtained under the same experimental condition (entry 2, Table 2). The system exhibits diastereoselectivity towards the *syn* isomer, typically leading to *syn*:*anti* molar ratios in the range from 65:35 to 78:22 using nitroethane as substrate.

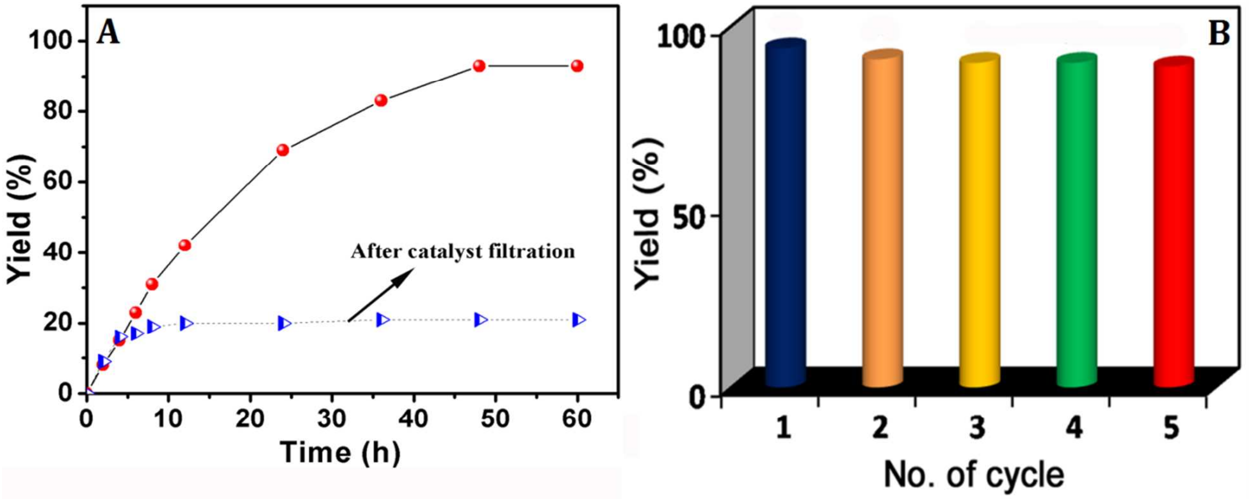
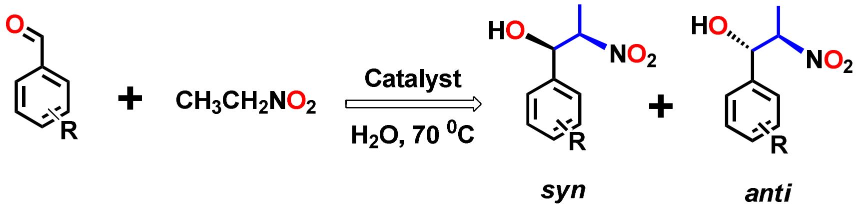


Fig. 5. (A) Plot of β-nitroalkanol yield *vs.* time for the Henry reaction of *p*-nitrobenzaldehyde and nitroethane with **1**. (B) Obtained yield in five consecutive reaction cycles employing **1** as catalyst.

A blank test with *p*-nitrobenzaldehyde was performed in the absence of any metal catalyst at 70 °C in aqueous medium, leading to *ca*. 11% conversion of *p*-nitrobenzaldehyde into β-nitroalkanol, after a reaction time of 48 h (Table 2, entry 7). The simple metal salts

$Zn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ and the ligand **HL** were also tested in water and the obtained reaction yields were much lower than that of catalyst **1** (Table 2, entries 8-10).



Scheme 2: Nitroaldol (Henry) reaction of benzaldehydes and nitroethane, with **1** or **2** as catalyst.

Table 2. Optimization of the parameters of the nitro-aldol reaction between *p*-nitrobenzaldehyde and nitroethane with **1** as catalyst[a].

Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	*T* (°C)	Solvent	Yield (%)[b]	Selectivity (*syn/anti)*[c]	TON[d]
1	**1**	48	3	70	H_2O	93	74 : 26	31
2	**2**	48	3	70	H_2O	90	65 : 35	30
3	**1**	48	3	70	CH_3CN	10	73 : 27	3.3
4	**1**	48	3	70	THF	25	74 : 26	8.3
5	**1**	48	3	70	MeOH	75	75 : 25	25
6	**1**	48	3	70	H_2O	93	74 : 26	31
7	Blank	48	-	70	H_2O	11	70:30	3.7
8	$Zn(NO_3)_2.6H_2O$	48	3	70	H_2O	18	82:18	6
9	$Cu(NO_3)_2. 3H_2O$	48	3	70	H_2O	22	81:19	7.3
10	**HL**	48	3	70	H_2O	28	78:22	9.3
11	**1**	48	1	70	H_2O	44	78:22	44
12	**1**	48	5	70	H_2O	92	74:26	18.4
13	**1**	48	7	70	H_2O	93	73:27	13.2

14	**1**	48	3	22 (RT)	H_2O	18	73:27	6
15	**1**	48	3	50	H_2O	77	78:22	25.7
16	**1**	48	3	100	H_2O	91	76:24	30.3
17	**1**	2	3	70	H_2O	8	76:24	2.6
18	**1**	4	3	70	H_2O	15	73:27	5
19	**1**	6	3	70	H_2O	23	74:26	7.7
20	**1**	8	3	70	H_2O	31	75:25	10.3
21	**1**	12	3	70	H_2O	42	78:22	14
22	**1**	24	3	70	H_2O	69	73:27	23
23	**1**	36	3	70	H_2O	82	73:27	27.3
24	**1**	48	3	70	H_2O	93	74:26	31
25	**1**	60	3	70	H_2O	93	75:25	31

[a] Reaction conditions: 3.0 mol% of catalyst **1** or **2** (mole corresponds to the repeating formula unit), benzaldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and water (2.0 mL) unless stated otherwise. [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.

The effect of catalyst **1** concentration (1 to 7 mol %), with all other parameters unchanged, was tested and the best yield was obtained in presence for 3 mol% of catalyst (Table 2, entry 1). A decrease in the catalyst loading from 3% to 1% led to a high decrease in the yield (Table 2, entry 11), but an increase in the catalyst loading did not have any significant effect (Table 2, entries 12-13).

We have also examined the effect of temperature. Its decrease below 70 ˚C resulted in an yield lowering (entries 1 and 14-15, Table 2). However, increase in the reaction temperature above 70 ˚C had no significant effect on the yield (entries 1 and 16, Table 2).

The effects of solvents other than water, such as methanol (MeOH), tetrahydrofuran (THF) and acetonitrile (CH_3CN), were also analyzed (Table 2, entries 3-6). Acetonitrile led to the lowest yield (*ca.* 10%), followed by THF (*ca*. 25%) and MeOH (*ca*. 75%). These yields are much lower than that (93%) obtained with water which appears as the best solvent.

Finally, under the optimized reaction conditions for **1** and *p*-nitrobenzaldehyde, a series of substituted benzaldehydes and aliphatic ones were examined, producing the corresponding β-nitroalkanols with yields ranging from 45 to 90% (Table 3). Aromatic aldehydes with electron-withdrawing groups i.e., *p*-chloro and *p*-fluoro substituent (entries 7-8, Table 3) lead to yields approaching that of the *p*-nitro substituent with a comparable diesteroselectivity. However, electron-donor substituents, as well as aliphatic aldehydes, provide lower reactivity and diastereoselectivity (entries 2-3 and 5-6, Table 3). Such observations are in accord with the expected electrophilic character of the aldehyde carbon towards the Henry reaction (see below).

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

Entry	Aldehyde	Yield (%)[b]	Selectivity[c] (*syn*/*anti*)	TON[d]
1	Benzaldehyde	77	78:22	25.6
2	*p*-anisaldehyde	45	76:24	15
3	*p*-methylbenzaldehyde	53	70:30	17.6
4	*m*-hydroxybenzaldehyde	61	78:22	20.3
5	Acetaldehyde	56	72:28	18.7
6	Propionaldehyde	62	69:31	20.7
7	*p*-chlorobenzaldehyde	87	78:22	29

8	*p*-fluorobenzaldehyde	90	76:24	30

[a]Reaction conditions: 3.0 mol% of catalyst **1**, aldehyde (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 ^{1}H NMR. [d] Number of moles of β-nitroalkanol per mole of catalyst.

To investigate the catalyst stability and reusability, we have carried out a recycling study using *p*-nitrobenzaldehyde and nitroethane as the model substrates, adopting the aforesaid optimized conditions. The catalyst **1** was recovered and reused in five consecutive runs, without any apparent loss of the catalytic activity [Fig. 5(B)]. Furthermore, the catalysts were found to be stable, retaining their structural integrity as evidenced from FT-IR spectra (Fig. S15) and powder XRD (Fig. S16, ESI), where no significant changes were observed after the reaction.

In order to test the possibility of catalyst leaching and the heterogeneity of the catalytic system, an experiment was performed following a procedure described by Sheldon *et al.*[15c] In our experiment, the catalyst **1** was removed by filtration from the mixture when the conversion was *ca.* 15% (after 4 h reaction time) followed by transferring the supernatant fluid and stirring for an additional 44 h under the same reaction conditions. As shown in Fig. 5(A), after removal of the catalyst by filtration, the conversion of benzaldehyde is almost negligible. These results evidence that the catalysis is heterogeneous in nature and no significant catalyst leaching occurs. Additionally, the potential leaching of the catalyst into the reaction mixture was also analyzed by ICP. For this purpose, the catalyst was removed by filtration after 48 h, the filtrated solution was evaporated to dryness and the residue was dissolved in HNO_3. The ICP analysis of the sample showed the presence of zinc in only *ca.* 0.02% of the amount used in the reaction, thus ruling out any significant leaching of the catalyst.

Table 4: Comparison of activities of MOFs as heterogeneous catalysts for the Henry reaction

with aldehyde and nitroethane.

Catalyst	Solvent/temp/time	Aldehyde	Yield (%)	Selectivity *syn:anti*	Reference
1	H_2O/70 °C/48 h	*p*-nitrobenzaldehyde	93	74:26	This paper
2	H_2O/70 °C/48 h	*p*-nitrobenzaldehyde	90	65:35	This paper
Zn(II) MOF with 4,4-bypyridine and 2-acetamidoterephthalic acid.	MeOH/70 °C/48 h	*p*-nitrobenzaldehyde	98	78 : 22	11*f*
Cu(II) MOF with pyridine carboxylates	Solvent free/70 °C/36 h	*p*-nitrobenzaldehyde	85	Not determined	24*a*
Zn(II) MOF with 1,3,5-tri(4-carboxyphenoxy)benzene	Solvent free/70 °C/72 h	*p*-nitrobenzaldehyde	15	Not determined	28*a*
Zn(II) MOF with terphenyl-3,3,-dicarboxylate and 1,4-diazabicyclo[2.2.2]octane (DABCO)	Solvent free/60 °C/120 h	*p*-nitrobenzaldehyde	34	Not determined	28*b*

In contrast to the previously reported heterogeneous catalysts (Table 4),[11f,24a,28] our catalysts have the advantages of being easy-to-prepare and operate preferably in aqueous medium producing high product yields.

The nitroaldol reaction generally involves the nucleophilic addition of a nitronate ion (which is generated *in situ* by the deprotonation of nitroalkane ligand by an external base or by the catalyst) to the aldehyde carbonyl group to give a β-hydroxynitroalkane.[11a,f,17f,18c,19a-c] The metal Lewis acid character and the basic environment provided by the amide backbone in the ligand framework are favourable to the nitroaldol reaction which occurs efficiently. The water solvent, in view of its amphoteric character, can also be involved in the deprotonation/protonation steps.

Conclusions

In conclusion, we have described the syntheses and characterization of two new novel metal organic frameworks of Zn(II) and Cu(II) (**1** and **2** respectively), using a new amide appended ligand **HL**. The single crystal X-ray diffraction analysis revealed **1** and **2** possess 2D and 3D dimensional structures, respectively. Further, the 2D framework of **1** contains a 3-fold interpenetration which is not observed in **2**. Topological analysis of **1** and **2** show a 6-connected pcu alpha-Po primitive cubic and a 8-connected body centred cubic (bcu) topology, respectively.

Both complexes **1** and **2** effectively catalyze the nitro-aldol reaction of aldehydes with nitroethane producing the corresponding β-nitroalkanols in high yields with a significant distereoselectivity in aqueous medium. To our knowledge, **1** and **2** provide the first examples of a Zn- or Cu-MOF heterogeneous catalyst for this reaction in water. The preferential use of water instead of an organic solvent is an important feature towards green catalysis for the preparation of simple nitro alcohols. In addition, the catalyst are highly stable and can be reused a number of times, without significant loss of catalytic property. They deserve to undergo further investigation as possible heterogeneous catalysts in other important types of organic reactions in aqueous medium.

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Supporting Information

Electronic Supplementary Information (ESI) available: CCDC deposition Nos. CCDC 1414611-1414612, experimental procedure, thermogravimetric analyses, Figs. S1-S16 containing FT-IR, ^{1}H and ^{13}C-NMR, powder XRD and Tables S1-S2.

References

1 (a) H. Zhou and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415; (b) M. D. Allendorf and V. Stavila, *CrystEngComm.*, 2015, **17**, 229.

2 (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keefee and O. M. Yaghi, *Science*, 2002, **295**, 469; (b) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350; (c) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.,* 2009, **38**, 1294.

3 (a) H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875; (b) C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158; (c) Y. B. He, W. Zhou, G. D. Qian, and B. L. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657; (d) J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.* 2014, **5**, 32; (e) Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schroder, *J. Am. Chem. Soc.*, 2009, **131**, 2159.

4 (a) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (b) A. Corma, H. Garcia and F. X. Llabre i Xamena, *Chem. Rev.*, 2010, **110**, 4606; (c) J. Rong. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869.

5 (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330; (b) J. Rocha, L. D. Carlos, F. A. Almeida Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926; (c) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126.

6 M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.

7 (a) R. Vaidhyanathan, D. Bradshaw, J. N. Rebilly, J. P. Barrio, J. A. Gould, N. G. Berry and M. J. Rosseinsky, *Angew. Chem. Int. Ed.*, 2006, **45**, 6495; (b) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, *Nature Mater.*, 2010, **9**, 172; (c) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.

8 A. C. McKinlay, R. E. Morris, P. Horcajada, G. Fe´rey, R. Gref, P. Couvreur and C. Serre, *Angew. Chem. Int. Ed.*, 2010, **49**, 6260.

9 (a) S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kiener and R. Moos, *Sensors* 2009, **9**, 1574; (b) J. D. Rocca and W. Lin, *Eur. J. Inorg. Chem.*, 2010, 3725. (c) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.

10 (a) Y. Y. Karabach, A. M. Kirillov, M. F. C. Guedes da Silva, M. N. Kopylovich and A. J. L. Pombeiro, *Cryst. Growth Des.,* 2006, **6**, 2200; (b) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402; (c) R. Banerjee, A. Phan, B.

Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939; (d) M. V. Kirillova, A. M. Kirillov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Eur. J. Inorg. Chem.*, 2008, 3423; (e) Y. Y. Karabach, A. M. Kirillov, M. Haukka, M. N. Kopylovich and A. J. L. Pombeiro, *J. Inorg. Biochem.,* **2008**, *102*, 1190; (f) S. Contaldi, C. Di Nicola, F. Garau, Y. Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, *Dalton Trans.*, 2009, 4928; (g) A. M. Kirillov, M. V. Kirillova and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2012, **256**, 2741; (h) T. C. O. Mac Leod, M. N. Kopylovich, M. F. C. Guedes da Silva, K. T. Mahmudov and A. J. L. Pombeiro, *Appl. Catal. A: Gen.* 2012, **439**, 15.

11 (a) M. N. Kopylovich, T. C. O. Mac Leod, K. T. Mahmudov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2011, **40**, 5352; (b) C. Pettinari, F. Marchetti, A. Cerquetella, R. Pettinari, M. Monari, T. C. O. Mac Leod, L. M. D. R. S. Martins and A. J. L. Pombeiro, *Organometallics*, 2011, **30**, 1616; (c) H. Naıli, F. Hajlaoui, T. Mhiri, T. C. O. Mac Leod, M. N. Kopylovich, K. T. Mahmudov and A. J. L. Pombeiro, *Dalton Trans.*, 2013, **42**, 399; (d) A. Karmakar, S. Hazra, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *New J. Chem.*, 2014, **38**, 4837; (e) M. Sutradhar, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Catal. Commun.*, 2014, **57**, 103; (f) A. Karmakar, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2014, **43**, 7795; (g) A. Karmakar, M. F. C. Guedes da Silva, S. Hazra and A. J. L. Pombeiro, *New J. Chem.*, 2015, **39**, 3004.

12 (a) K. Schlichte, T. Kratzke and S. Kaskel, *Microporous Mesoporous Mater.*, 2004, **73**, 81; (b) F. Vermoortele, M. Vandichel, B. Van de Voorde, R. Ameloot, M. Waroquier, V. Van Speybroeck and D. E. de Vos, *Angew. Chem., Int.*

Ed., 2012, **51**, 4887; (c) S. Horike, M. Dinca, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854; (d) A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192; (e) P. Horcajada, S. Surble, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki and G. Ferey, *Chem. Commun.*, 2007, 2820; (f) L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos, *Chem. Eur. J.*, 2006, **12**, 7353; (g) F. G. Cirujano, F. X. Llabre´ s i Xamena and A. Corma, *Dalton Trans.,* 2012, **41**, 4249.

13 (a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (b) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607.

14 (a) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem., Int. Ed.*, 2008, **47**, 4144; (b) M. Savonnet, S. Aguado, U. Ravon, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel and D. Farrusseng, *Green Chem.*, 2009, **11**, 1729; (c) Q. R. Fang, D. Q. Yuan, J. Sculley, J. R. Li, Z. B. Han and H. C. Zhou, *Inorg. Chem.*, 2010, **49**, 11637; (d) P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *Chem. Mater.*, 2011, **23**, 2565; (e) S. Aguado, J. Canivet and D. Farrusseng, *J. Mater. Chem.*, 2011, **21**, 7582.

15 (a) C. Perego, A. Carati, P. Ingallina, M. A. Mantegazza and G. Bellussi, *Appl. Catal. A: Gen.*, 2001, **221**, 63; (b) A. Corma, L. T. Nemeth, M. Renz and S. Valencia, Nature, 2001, **412**, 423; (c) R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, *Acc. Chem. Res.*, 1998, **31**, 485; (d) A. Corma, M. E. Domine and S. Valencia, *J. Catal.*, 2004, **215**, 294; (e) Y. Zhu, G. Chuah and S. Jaenicke, *J. Catal.*,

2004, **227**, 1; (f) M. F. C. Guedes da Silva, A. J. L. Pombeiro, *"*Redox Potential-Structure and Parameterization Relationships in the Characterization and Identification of Organometallic Compounds", in "Advances in Organometallic Chemistry and Catalysis" (The Silver/Gold Jubilee ICOMC Celebratory Book), A. J. L. Pombeiro (ed.), J. Wiley & Sons, 2014, Chapter 50, pp. 677.

16 (a) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui and G. Qian, *Angew. Chem., Int. Ed.*, 2009, **48**, 500; (b) B. Zheng, J. Bai, J. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748; (c) J. Duan, Z. Yang, J. Bai, B. Zheng, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 3058; (d) B. Zheng, Z. Yang, J. Bai, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 7025.

17 (a) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.* 1962, **84**, 571; (b) H. A. Bent, *Chem. Rev.*1968, **68**, 587; (c) P. L. Huyskens, *J. Am. Chem. Soc.,* 1977, **99**, 2578; (d) M. Shibasaki and H. Groger, in Comprehensive Asymmetric Catalysis, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, Berlin, Germany, 1999, pp. 1075; (e) M. Shibasaki, H. Groger and M. Kanai, in Comprehensive Asymmetric Catalysis, Supplement 1, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, Heidelberg, Germany, 2004, pp. 131; (f) J. Boruwa, N. Gogoi, P. P. Saikia and N. C. Barua, *Tetrahedron: Asymmetry*, 2006, **17**, 3315; (g) C. Palomo, M. Oiarbide and A. Laso, *Eur. J. Org. Chem.*, 2007, 2561.

18 (a) M. Shibasaki, M. Kanai, S. Matsunaga and N. Kumagai, in Bifunctional Molecular Catalysis, ed. T. Ikariya and M. Shibasaki, 2011, pp. 1-30, ch. 37; (b) C. Palomo, M. Oiarbide and A. Mielgo, *Angew. Chem., Int. Ed.*, 2004, **43**, 5442; (c) S. Jammi and T.

Punniyamurthy, *Eur. J. Inorg. Chem.*, 2009, 2508; (d) S. Jammi, M. A. Ali, S. Sakthivel, L. Rout and T. Punniyamurthy, *Chem.-Asian J.*, 2009, **4**, 314; (e) P. Chintala, S. K. Ghosh, E. Long, A. D. Headley and B. Nia, *Adv. Synth. Catal.*, 2011, **353**, 2905; (f) G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha and Z. Wang, *Chem.-Eur. J.*, 2011, **17**, 1114.

19 (a) A. Das, R. I. Kureshya, K. J. Prathap, M. K. Choudhary, G. V. S. Rao, N. H. Khana, S. H. R. Abdi and H. C. Bajaj, *Appl. Catal.*, A, 2013, **459**, 97; (b) N. Qi, R.-Z. Liao, J.-G. Yu and R.-Z. Li, *J. Comp. Chem.* , 2009, **31**, 1376; (c) A. Bulut, A. Aslan and O. Dogan, *J. Org. Chem.*, 2008, **73**, 7373; (d) R. Kowalczyk, L. Sidorowicz and J. Skarzewski, *Tetrahedron: Asymmetry*, 2007, **18**, 2581.

20 (a) V. J. Bulbule, V. H. Deshpande, S. Velu, A. Sudalai, S. Sivasankar and V. T. Sathe, *Tetrahedron*, 1999, **55**, 9325; (b) R. Maggi, D. Lanari, C. Oro, G. Sartori and L. Vaccaro, *Eur. J. Org. Chem.*, 2011, 5551; (c) T. Nitabaru, A. Nojiri, M. Kobayashi, N. Kumagai and M. Shibasaki, *J. Am. Chem. Soc.*, 2009, **131**, 13860.

21 (a) F. A. Luzzio, *Tetrahedron*, 2001, **57**, 915; (b) A. V. Davis, M. Driffield and D. K. Smith, *Org. Lett.*, 2001, **3**, 3075; (c) J. M. Concellon, H. R. Solla and C. Concellon, *J. Org. Chem.*, 2006, **71**, 7919; (d) T. Jiang, H. X. Gao, B. X. Han, G. Y. Zhao, Y. H. Chang, W. Z. Wu, L. Gao and G. Y. Yang, *Tetrahedron Lett.*, 2004, **45**, 2699; (e) J. A. Weeden and J. D. Chisholm, *Tetrahedron Lett.*, 2006, **47**, 9313.

22 (a) A. C. Forsyth, R. M. Paton and I. Watt, *Tetrahedron Lett.*, 1989, **30**, 993; (b) F. A. Luzzio and R. W. Fitch, *Tetrahedron Lett.*, 1994, **35**, 6013; (c) A. Cwik, A. Fuchs, Z.

Hella and J. Clacens, *Tetrahedron*, 2005, **61**, 4015; (d) D. Simoni, F. P. Invidiata, S. Manfredini, R. Ferroni, I. Ampronti and G. P. Pollini, *Tetrahedron Lett.*, 1997, **38**, 2749; (e) X. Wang and S. Cheng, *Catal. Commun.*, 2006, **7**, 689; (f) V. J. Mayani, S. H. R Abdi, R. I. Kureshy, N. H. Khan, A. Das and H. C. Bajaj, *J. Org. Chem.*, 2010, **75**, 6191; (g) G. Madhavi, S. J. Kulkarni, K. R. Murthy, V. Viswanathan and K. V. Raghavan, *J. Porous. Mater*, 2007, **14**, 433; (h) C. Murugan, H. C. Bajaj and R. V. Jasra, *Catal. Lett.*, 2010, **137**, 224; (i) M. A. Khalilzadeh, A. Hosseini and A. Pilevar, *Eur. J. Org. Chem.*, 2011, 1587; (j) B. Basudeb, P. Das and S. Das, *Curr. Org. Chem.*, 2008, **12**, 14118; (k) W. Xie and X. Huang, *Catal. Lett.*, 2006, **107**, 53; (l) L. Kurti and B. Czako, Strategic Applications of Named Reactions in Organic synthesis, (Elsevier Academic Press M A, Burlington), 2005.

23 (a) M. N. Kopylovich, A. Mizar, M. F. C. Guedes da Silva, T. C. O. Mac Leod, K. T. Mahmudov and A. J. L. Pombeiro, *Chem. Eur. J.*, 2013, **19**, 588; (b) K. T. Mahmudov, M. N. Kopylovich, M. Haukka, G. S. Mahmudova, E. F. Esmaeila, F. M. Chyragov and A. J. L. Pombeiro, *J. Mol. Struct.*, 2013, **1048**, 108; (c) S. Hazra, A. Karmakar, M. F. C. Guedes da Silva, L. Dlháň, R. Boča and A. J. L. Pombeiro, *New J. Chem.*, 2015, **39**, 3424; (d) B. G. M. Rocha, T. C. O. Mac Leod, M. F. C. Guedes da Silva, K. V. Luzyanin, L. M. D. R. S. Martins and A. J. L. Pombeiro, *Dalton Trans.*, 2014, **43**, 15192.

24 (a) L. X. Shi and C. D. Wu, *Chem. Commun.*, 2011, **47**, 2928; (b) D. D. Qin, W. H. Lai, D. Hu, Z. Chen, A. A. Wu, Y. P. Ruan, Z. H. Zhou and H. B. Chen, *Chem.- Eur. J.*, 2012, **18**, 10515; (c) B. Ni and J. He, *Tetrahedron Lett.*, 2013, **54**, 462; (d) E. Wolinska,

Tetrahedron, 2013, **69**, 7269; (e) Z. Kałuza, K. Bielawski, R. C´ wiek, P. Niedziejko and P. Kaliski, *Tetrahedron: Asymmetry*, 2013, **24**, 1435.

25 R. Ballini, G. Bosica and P. Forconi, *Tetrahedron*, 1996, **52**, 1677.

26 N. Neelakandeswari, G. Sangami, P. Emayavaramban, R. Karvembu, N. Dharmaraj and H. Y. Kim, *Tetrahedron Lett.*, 2012, **53**, 2980.

27 K. K. Sharma, A. V. Biradar, S. Das and T. Asefa, *Eur. J. Inorg. Chem.*, 2011, 3174.

28 (a) X. M. Lin, T. T. Li, Y. W. Wang, L. Zhang and C. Y. Su, *Chem. Asian J.*, 2012, **7**, 2796; (b) J. M. Gu, W. S. Kim and S. Huh, *Dalton Trans.*, 2011, **40**, 10826; (c) P. W. Siu , Z. J. Brown, O. K. Farha, J. T. H. and K. A. Scheidt, *Chem. Commun.,* 2013, **4 9**, 10920.

29 (a) J. A. L. da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.,* 2011, **255**, 2232; (b) L. M. D. R. S. Martins and A. J. L. Pombeiro, *Coord. Chem. Rev.,* 2014, **265**, 74; (c) A. J. L. Pombeiro, in: *Advances in Organometallic Chemistry and Catalysis*, ed. A. J. L. Pombeiro, John Wiley & Sons, Inc., Hoboken, NJ, USA. 2013, Ch. 2, 15.

30 (a) L. Gonsalvi and M. Peruzzini, Chapter 7. "Aqueous Phase Reactions Catalysed by Transition Metal Complexes of 7-phospha-1,3,5-triazaadamantane (PTA) and derivatives" in *Phosphorus compounds: advanced tools in catalysis and material sciences* (Eds M. Peruzzini, L. Gonsalvi), Catalysis by Metal Complexes series, 1st Edition, Vol. 37, Springer (London) 2011; (b) F.´ Joo, Aqueous Organometallic Catalysis; Kluwer: Dordrecht, 2001; (c) Catalytic rearrangements and allylation reactions in water, in *Metal-Catalyzed Reactions in Water.* V. Cadierno, J. García-Álvarez, S. E.

García-Garrido, *Wiley-VCH (Eds. P. H. Dixneuf, V. Cadierno)*, 2013, 243; (d) T. Kitanosonoa and S. Kobayashi, *Adv. Synth. Catal.*, 2013, **355**, 3095; (e) H. Gong, H. Zeng, F. Zhou and C. J. Li, *Angew. Chem. Int. Ed.,* 2015, **54**, 5718; (f) S. N. Arbuzova, N. K. Gusarova, S. I. Verkhoturova, T. I. Kazantseva, Igor A. Ushakov, A. G. Mal'kina, and B. A. Trofimov, *Hetero. Chem.*, 2015, **26**, 3; (g) S. Keesara, M. R. Mandapati and S. Parvathaneni, *App. Catal. A: Gen*, 2015, **496**, 58; (h) A. K. Rathi, M. B. Gawande, R. Zboril and R. S. Varma, *Coord. Chem. Rev.*, 2015, **291**, 68.

31 D. D. Perrin, W. L. F. Armango and D. R. Perrin, *Purification of Laboratory Chemicals*; Pergamon: Oxford, U.K. **1986**.

32 K. Splith, I. Neundorf, W. Hu, H. W. P. N'Dongo, V. Vasylyeva, K. Merzb and U. Schatzschneider, *Dalton Trans.*, 2010, **39**, 2536.

33 (a) Bruker, *APEX2 & SAINT, AXS Inc.*, 2007 Bruker AXS Inc., Madison, Wisconsin, USA; (b) G. M. Sheldrick, *ActaCryst.,* 2008, A**64**, 112; (c) A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115; (d) L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849; (e) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466; (f) A.L. Spek. *ActaCryst.,* 2009, D**65**, 148.

34 H. L. Hsiao, C. J. Wu, W. Hsu, C. W. Yeh, M. Y. Xie, W. J. Huang and J. D. Chen, *CrystEngComm.*, 2012, **14**, 8143.

35 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* 1984, 1349.

36 (a) M. O'Keeffe and O. M. Yaghi, *Reticular Chemistry Structure Resource*, Arizona State University, Tempe, AZ, 2005, http://rcsr.anu.edu.au/; (b) V. A. Blatov, *IUCr, Comput. Comm. Newslett*., 2006, **7**, 4, http://www.topos.ssu.samara. ru/; (c) V. A. Blatov, *Struct. Chem.,* 2012*,* **23***,* 955.

Table 1: Crystal data and structure refinement details for compounds **1** and **2.**

Identification name	**1**	**2**
Formulae	$C_{40}H_{36}N_6O_{12}Zn_2$	$C_{38}H_{48}CuN_8O_{11}$
Mol. wt.	923.49	856.38
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
Temperature /K	296 (2)	150(2)
Wavelength /Å	0.71073	0.71073
a /Å	8.0350(9)	8.3259(14)
b /Å	24.892(3)	22.773(4)
c /Å	10.8856(13)	20.105(3)
α/°	90	90
β/°	111.560(4)	93.700(5)
γ/°	90	90
V/ Å^3	2024.9(4)	3804.1(11)
Z	2	4
Density/Mgm^{-3}	1.515	1.495
Abs. Coeff. /mm^{-1}	1.255	0.648
F(000)	948	1796.0
Refl. collected	46996	43898
Refl. unique	7404	6972
Max. 2θ/°	25.372	25.40
Ranges (h, k, l)	-9<= h <= 9 -30<= k <= 30 -13<= l <= 13	-10<= h <= 10 -27<= k <= 27 -24<= l <= 24
Complete to 2θ (%)	99.8	98.5
Refl. with I > 2σ(I)	7306	4604
Data/ Restraints/Parameters	7404/1/552	6972/80/360
Goof (F^2)	1.109	1.057
R1 [I > 2s(I)]	0.0318	0.0834
wR2 [I > 2s(I)]	0.0795	0.2110
R1 [all data]	0.0322	0.1243
wR2 [all data]	0.0801	0.2268