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ARTICLE TYPE

# A 3-D diamondoid MOF catalyst based on in-situ generated [Cu(L)<sub>2</sub>] N-heterocyclic carbene (NHC) linkers: hydroboration of CO<sub>2</sub>

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A new MOF, [Zn<sub>4</sub>O{Cu(L)<sub>2</sub>}<sub>2</sub>] (**1**), with a 4-fold interpenetrated 3D diamondoid structure was synthesised from in-situ generated [Cu(L)<sub>2</sub>] NHC linkers. MOF **1** possesses tetrahedral Zn<sub>4</sub>O nodes, which are unusually coordinated by four pairs of carboxylates from four [Cu(L)<sub>2</sub>] linkers, and 14 Å 1-D pore channels lined with [Cu(L)<sub>2</sub>] moieties that catalyse the hydroboration of CO<sub>2</sub>.

Metal-organic frameworks (MOFs) are a class of porous materials with potential applications in gas storage,<sup>1</sup> molecular separations<sup>2</sup> and catalysis.<sup>3</sup> MOFs are constructed via a modular approach from metal salts and organic linkers that allows their structures and functionality to be systematically modified.<sup>4</sup> Such chemical mutability enables the properties of a given material to be tailored for a particular application. This feature, in conjunction with large pore volumes and high surface areas,<sup>4</sup> has particularly earmarked MOFs as promising materials for heterogeneous catalysis.<sup>3</sup> One approach to developing catalytic MOFs relies upon embedding established catalytic moieties into the framework.<sup>3, 5</sup> In this regard, post-synthetic metalation is a promising strategy that provides a route for encapsulating existing homogenous catalysts within the pore network or anchoring them to the MOF structure.<sup>5b</sup> Regarding this latter approach, a number of MOFs have been generated that contain sites, such as diols,<sup>6</sup> cyclometalation sites,<sup>7</sup> and heterocyclic donors,<sup>8</sup> with potential for post-synthetic catalytic metal inclusion.

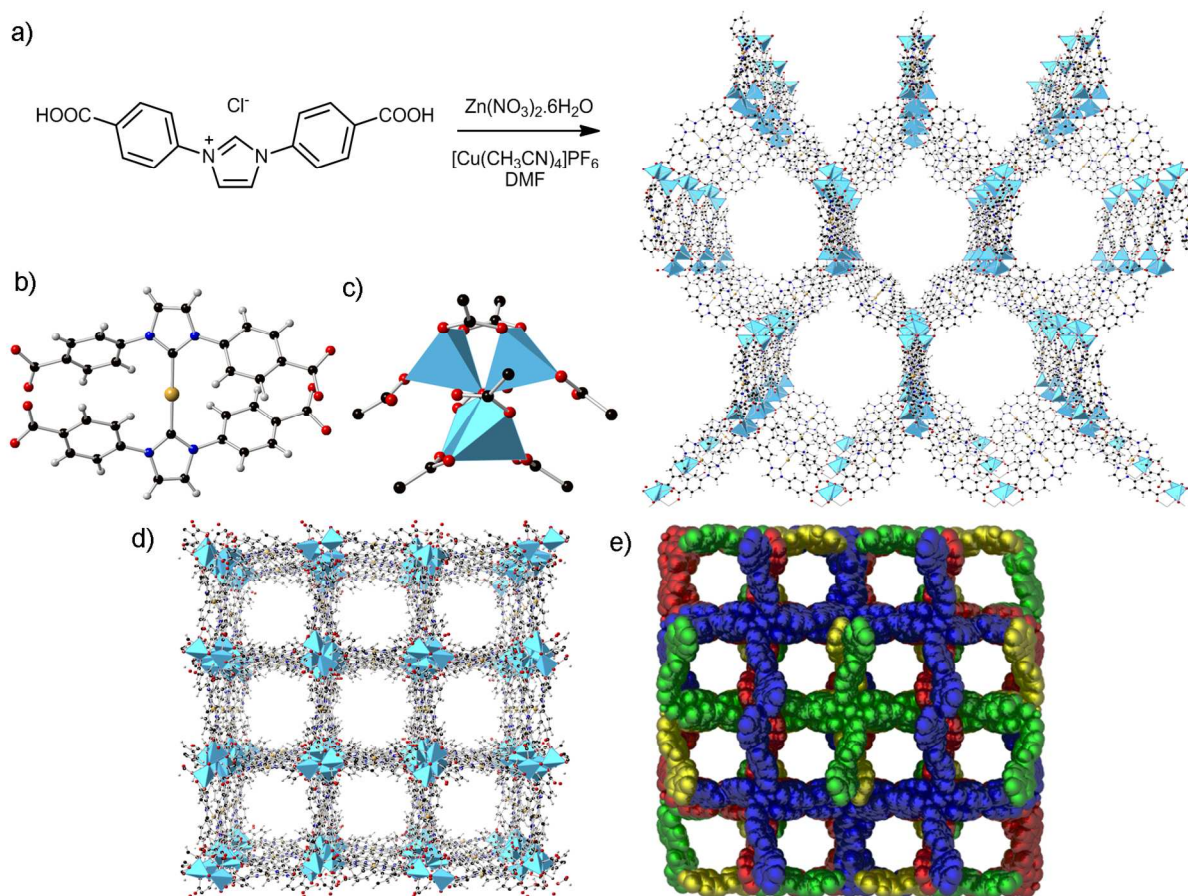
The use of azolium-containing linkers that are precursors to N-heterocyclic carbene (NHC) complexes has also been identified as a route for preparing MOF catalysts.<sup>9-11</sup> Such species are attractive components for MOFs as they are ubiquitous stabilising ligands for catalytic metals. Azolium linkers have been directly employed in MOF synthesis<sup>12</sup> and, in some cases, post-synthetic metalation used to convert these to NHC complexes inside the MOF.<sup>9</sup> Alternatively, Yaghi and co-workers have shown that pre-formed NHC complexes can be utilized as framework links.<sup>10</sup> Furthermore, NHC complex generation concomitant with MOF synthesis has been reported.<sup>11</sup> In these examples the NHC complex is appended to the framework and protrudes into the available pore space. Here, we report the first example of a MOF ([Zn<sub>4</sub>O{Cu(L)<sub>2</sub>}<sub>2</sub>], **1**) that uses a bis(N-heterocyclic) complex ([Cu(L)<sub>2</sub>], L = NHC) as a structural element. In addition to limiting the pore volume occupied by the catalytic sites and

ensuring full occupancy of the catalytic metal, the unusual geometric arrangement yields a diamond-like 3-D framework. This 3D network is constructed from Zn<sub>4</sub>O nodes that adopt an uncommon coordination environment surrounded by four pairs of ligands. MOF **1** has a 4-fold interpenetrated structure with large 1D channels (limiting pore dimension of ~8.4 Å) and walls comprised of the [Cu(L)<sub>2</sub>] links. The [Cu(L)<sub>2</sub>] links of **1**, like related homogenous counterparts, were found to be active catalysts for the hydroboration of CO<sub>2</sub>.<sup>13</sup>

[Zn<sub>4</sub>O{Cu(L)<sub>2</sub>}<sub>2</sub>] (**1**) was synthesised in 59% yield by solvothermal treatment of H<sub>3</sub>LCl with one equivalent of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and half an equivalent of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> in DMF at 120°C over 14 days (Figure 1a). This provided X-ray quality, pale yellow crystals of **1**. Cu<sub>2</sub>O can also be employed as a Cu(I) source for MOF **1** synthesis<sup>11</sup> but in our hands gave mixtures containing residual Cu<sub>2</sub>O that were challenging to separate. Crystalline samples synthesised using both routes readily matched the powder X-ray diffraction (PXRD) pattern simulated from the single crystal data (Figure 2) and dried samples gave satisfactory EDX and elemental analyses.<sup>†</sup>

Single crystal X-ray crystallography revealed that **1** has a diamondoid 3D framework (Figure 1a). This is formed from a Zn<sub>4</sub>O structural node possessing a novel coordination mode and the first example of an *in-situ* generated [Cu(L)<sub>2</sub>] (Cu(I) bis-NHC) linker. Due to the presence of four pairs of ligands around the Zn<sub>4</sub>O node (i.e. four [Cu(L)<sub>2</sub>] linkers), the cluster acts as a tetrahedral rather than octahedral structural unit (Figure 2c). Four carboxylate groups adopt the coordinating mode seen in the IRMOF series<sup>14</sup> but an additional carboxylate that is held in close proximity to the first in each [Cu(L)<sub>2</sub>] entity also coordinates in a monodentate fashion to each node. The bond lengths and angles about the Zn(II) centres are typical but with the coordination requirements of eight carboxylate groups leading to the presence of four chelating carboxylates and four monodentate donors. The Zn<sub>4</sub>O node is not strictly tetrahedral but flattened slightly with Cu-Zn-Cu angles of 93.5, 95.0, 120.4 and 114.9°.

During MOF synthesis the imidazolium link H<sub>3</sub>L undergoes deprotonation and conversion to its NHC form. Such reactions can require the addition of a strong base but it has previously been shown that Cu(I) NHC entities are formed concomitantly with MOF synthesis,<sup>11</sup> although this is the first report of the formation of a bis-NHC ligand. NHC complex formation during MOF synthesis is facile because basic species such as

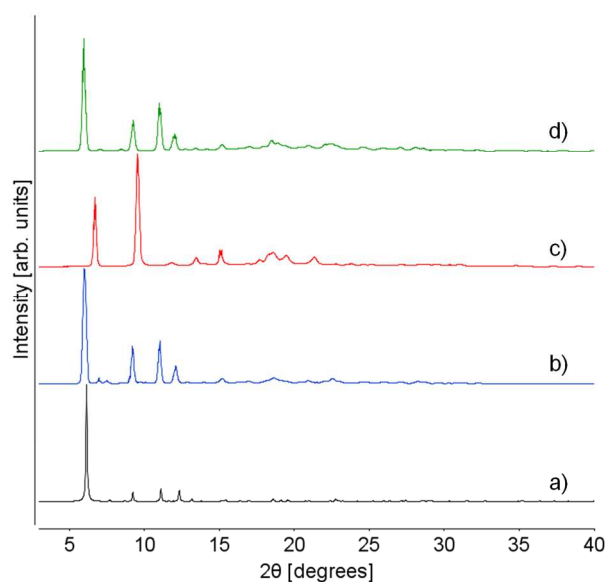


**Figure 1.** a) Synthesis of  $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$  (**1**) and a perspective view of one diamond-like net of the structure down the *a*-axis. b) The  $[\text{Cu}(\text{L})_2]$  bis-NHC link, c) the unusual coordination of the  $\text{Zn}_4\text{O}$  node in **1**, and views of the four-fold interpenetrated structure down the *b*-axis in d) ball and stick or e) space-filling representations. For a)-d): zinc - cyan, copper(I) - gold, carbon - black, nitrogen - blue, oxygen - red, hydrogen - white; for e): each framework is shown a single colour (red, green, yellow and blue).

dimethylamine are formed in situ via DMF decomposition.<sup>15</sup> One of the  $[\text{Cu}(\text{L})_2]$  moieties (Figure 1b) adopts an essentially planar conformation that is not normally seen for free  $[\text{Cu}(\text{NHC})_2]$  species<sup>16</sup> with N-C-Cu-C torsion angles around Cu4 being 15.7 and 16.1° (the other linker shows a greater twist with a torsion angles of 76.7 and 81.0° but still a relatively flat conformation). This brings the carboxylate donors of the pairs of NHCs into close proximity and favours the unusual coordination of the  $\text{Zn}_4\text{O}$  node. The unusual geometry observed for  $[\text{Cu}(\text{L})_2]$  can be attributed to its confinement within the MOF architecture.

The combination of a tetrahedral node and the topologically trivial  $[\text{Cu}(\text{L})_2]$  links generates a diamondoid framework (Figure 1a). The MOF is four-fold interpenetrated (Figures 1d and 1e) which produces a material with *ca.* 14 Å channels parallel to the *b*-axis with an octagonal cross-section. These channels are lined with exposed  $[\text{Cu}(\text{L})_2]$  moieties that act as the channel walls. The Cu-Cu distances across the channel and to a Cu centre perpendicular to the first are *ca.* 14 and 9.6 Å respectively.

Thermogravimetric analysis of a sample of **1** indicated that after solvent loss the material is thermally stable up until 400°C (Figure S3). Furthermore, PXRD experiments on solvent exchanged samples indicated that the material is stable to a range of solvents (DMF, dichloromethane, and THF). Despite its thermal stability, drying a sample of **1** at room temperature under



**Figure 2.** PXRD patterns of  $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$  (**1**): a) simulated from the single crystal data, b) as-synthesised, c) dried, and d) after one catalytic cycle.

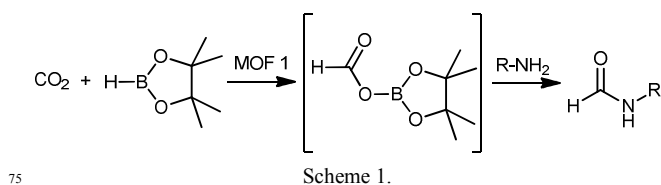
vacuum led to a significant change in the PXRD pattern (Figure 1c). Zn<sub>4</sub>O clusters can be hydrolytically unstable and prone to structure collapse upon desolvation.<sup>17</sup> In **1** the unusual monodentate coordination mode for four of the carboxylates may predispose the material toward a structural rearrangement. A 77 K N<sub>2</sub> isotherm confirmed that the structure of the desolvated material is not accessible to this probe molecule (despite a calculated surface area of ~1300 m<sup>2</sup>/g). Nonetheless, the material can be resolvated by heating **1** at 85°C in DMF for 24 h and PXRD reveals the as-synthesised structure to be partially regained (Figure S2). Structural recovery upon desolvation/resolvation cycles is not uncommon in MOF chemistry.<sup>18</sup>

A survey of the literature indicates that Zn forms a number of common SBUs with carboxylate ligands, including three- and four-bladed dinuclear paddlewheels,<sup>19</sup> Zn<sub>4</sub>O tetrahedra,<sup>14</sup> and infinite 1-D Zn chains.<sup>20</sup> More recently, examples of higher nuclearity SBUs have been observed with Zn, including Zn<sub>6</sub>O<sub>2</sub><sup>21</sup> and Zn<sub>8</sub>O clusters,<sup>12g</sup> the latter of which forms from the same imidazolium link (H<sub>3</sub>LCl) under different conditions. In the present example charge balance of the resulting framework appears to be an important driving force for the formation of the MOF. For example, attempts to prepare a palladium(II) chloride containing analogue of **1** were not successful, consistent with a different charge on the in situ generated link (i.e. [Cu(L)<sub>2</sub>]) has an overall -3 charge whereas [PdCl<sub>2</sub>(L)<sub>2</sub>] would have a -4 charge).

Relatively few MOFs comprised of NHC ligands have been assessed for their catalytic performance.<sup>9</sup> Accordingly, we sought to investigate the potential of **1** to activate CO<sub>2</sub> via hydroboration.<sup>13</sup> In addition to hydroboration of CO<sub>2</sub>, copper(I) NHC complexes are also known to catalyse reactions such as the azide-alkyne “click chemistry”<sup>22</sup> and the hydrosilylation of ketones.<sup>16a, 23</sup> Of interest is that the cationic bis(NHC) complexes generally have improved catalytic activity by comparison with their neutral mono(NHC) parent.<sup>16a, 22b</sup> The CO<sub>2</sub> hydroboration reactions (Scheme 1) were conducted in THF at 35°C under CO<sub>2</sub> atmosphere (1 atm) in the presence of pinacolborane and different amounts of MOF **1** (Table 1) as the catalyst. The product HCO<sub>2</sub>B(pin) was not isolated, but instead immediately used as a formylating reagent for benzylamine<sup>13</sup> after the MOF catalyst was removed by filtration. Almost quantitative conversion was obtained when 10 or 5 mol% of **1** was used (entries 2 and 3, respectively) whereas 66% of conversion was observed when only 1 mol% was employed (entry 4). These results are similar to data previously obtained involving a related homogeneous catalyst Cu(O*t*-Bu)(IPr) (entry 5).<sup>13</sup>

Crystals of **1** can be readily recovered after the reaction and no significant structural changes were observed in the PXRD pattern (Figure S6). An important aspect of using a MOF based NHC as a heterogeneous catalyst is that the MOF can be recovered from the reaction medium. We also assessed recyclability of the catalyst by using a 5 mol% loading of **1** over five cycles (Table S3). These experiments revealed that the catalytic activity of **1** decreased over the first two cycles and then stabilised at about 50% conversion thereafter. PXRD analysis of **1** after the fifth cycle clearly showed that the structure is retained (Figure S6), but the broadness and reduced intensity of the PXRD peaks indicate diminished crystallinity. Inductively-coupled plasma mass

spectrometry (ICP-MS) measurements (Table S4) of the reaction mixture after the first catalytic cycle indicated that a very small amount of copper (0.023%, 50±2 ppb) leaches from **1** during the course of the catalytic reaction. The copper leakage from MOF **1** can be rationalised on the basis of proposed mechanisms for catalytic reactions involving Cu(I) bis-NHC complexes, which involve de-coordination of at least one NHC ligand during the catalytic cycle.<sup>13, 22, 23</sup> The regeneration of the starting Cu(I) bis-NHC moieties within MOF **1** requires re-coordination of one NHC ligand. Based on the minor loss of copper during the catalytic cycle, as measured by ICP-MS, regeneration is not quantitative and, most likely, disfavoured at the crystal surface where the NHC link is less spatially constrained than within the centre of the framework. This may be the origin of the slightly depressed catalytic activity shown in subsequent reactions.



**Table 1.** N-Formylation of benzylamine using HCO<sub>2</sub>B(pin) prepared by a [Zn<sub>4</sub>O{Cu(L)<sub>2</sub>}]<sub>2</sub>-catalysed hydroboration of CO<sub>2</sub>.

entry	Cu catalyst	mol % Cu	conv. (%) <sup>a</sup>
1	none	0	6
2	[Zn <sub>4</sub> O{Cu(L) <sub>2</sub> }] <sub>2</sub>	10 <sup>b</sup>	92
3	[Zn <sub>4</sub> O{Cu(L) <sub>2</sub> }] <sub>2</sub>	5 <sup>b</sup>	92
4	[Zn <sub>4</sub> O{Cu(L) <sub>2</sub> }] <sub>2</sub>	1 <sup>b</sup>	66
5 (ref. 13)	Cu(O <i>t</i> -Bu)(IPr)	10	98

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>b</sup> 1 mol % Cu = 0.5 mol % MOF

Our preliminary catalytic studies indicate that MOF **1** acts to heterogeneously catalyse the hydroboration of CO<sub>2</sub>. Examination of the catalysis reaction solution shows no evidence of a homogenous NHC species<sup>‡</sup> being present in solution (excepting a very small amount of copper). On this basis, and due to the data obtained from recycling experiments, we can be confident the material is not a supplier of a homogenous catalyst species for the reaction. Additional evidence for this conclusion comes from additional catalytic experiments we have briefly investigated, namely “click chemistry” and hydrosilylation reactions, where we observed that the MOF does not catalyse these reactions. This observation we attribute to increased molecular size of the reactants involved and heterogeneous nature of this MOF catalyst.

In conclusion, we have reported the first example of a MOF comprising a Cu(I) bis-NHC ligand catalytic site. This entity is formed in-situ from an azolium ligand and a Cu(I) source. The ‘pairing’ of ligands in the MOF generates an unusual Zn<sub>4</sub>O SBU and a structurally flexible diamonded 3D network. As the Cu(I) bis-NHC site is a structural building block the catalytic sites are well defined and the MOF shows similar catalytic behaviour to related homogenous Cu(I) NHC species yet has the advantage of being a heterogeneous system that can be recovered following a reaction. Our results show for the first time that catalysis by bis-NHC species within a MOF is possible however, a more robust

framework will be required to realise the full potential of these moieties.

## Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis and characterisation of MOF 1, further details of X-ray crystallography and catalysis results. See DOI: 10.1039/b000000x/

‡ In some instances MOFs are known to catalyse reactions via dissolution to produce homogenous chemical species.<sup>3</sup> In this case we believe that the evidence presented for MOF 1 indicates that the material remains intact and acts as a heterogenous catalyst although, like many systems, we cannot entirely rule out the presence of a highly active homogenous entity.

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Electronic Supplementary Information

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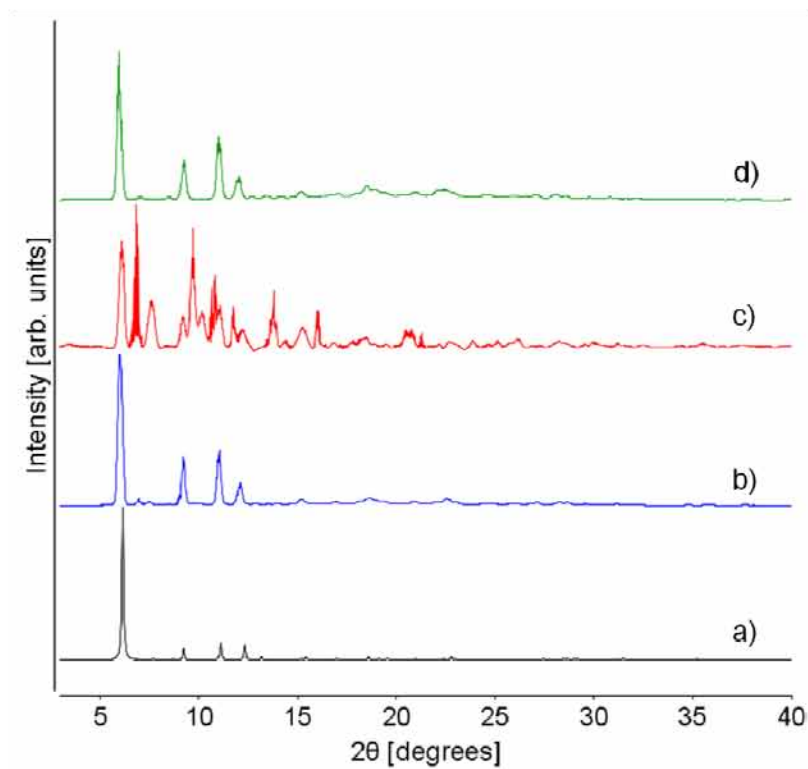
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## 1. General experimental details

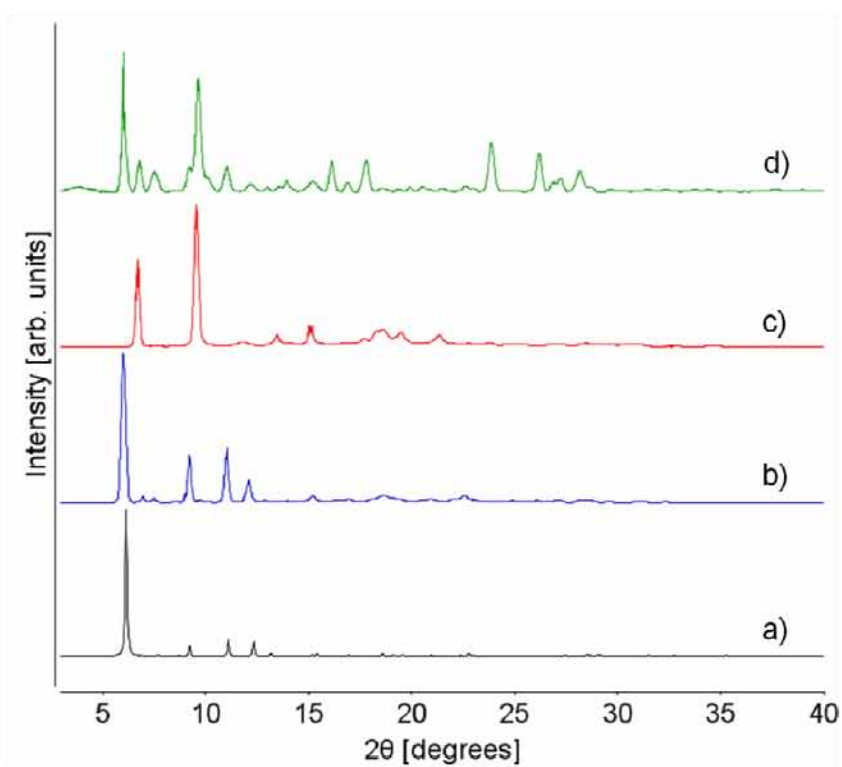
Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago (North Dunedin, New Zealand). Infrared spectra were collected on a Perkin-Elmer Spectrum 100 using a UATR sampling accessory. NMR spectra were recorded on a Varian Gemini 300 MHz or a 500 MHz NMR spectrometer at 23 °C using a 5 mm probe. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer STA-6000 instrument under a constant flow of N<sub>2</sub> at a temperature increase rate of 10 °C/min. Powder X-ray diffraction data were collected on a Rigaku Hiflux Homelab system using Cu K $\alpha$  radiation with an R-Axis IV++ image plate detector. Samples were mounted on plastic loops using paratone-N and data collected by scanning 90° in  $\Phi$  for 120 s exposures. The data were converted into xye format using the program Datasqueeze 2.2.2, Datasqueeze Software; Wayne, Pennsylvania, U.S.A., 2010. Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.0. Energy-dispersive X-ray spectroscopy (EDX) was performed on a Philips XL30 field emission scanning electron microscope. Catalytic reactions were carried out with standard Schlenk techniques under argon. THF was distilled from sodium/benzophenone. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. **H<sub>3</sub>LCI**<sup>1</sup> and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub><sup>2</sup> were prepared according to the methods described in the literature.

## 2. Synthesis of [Zn<sub>4</sub>O{Cu(L)<sub>2</sub>}<sub>2</sub>] (1)

**H<sub>3</sub>LCI** (20 mg, 0.058 mmol), Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (17.3 mg, 0.058 mmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (10.8 mg, 0.029 mmol) were combined and dissolved in DMF (5 mL) in a 20 mL glass vial with a Teflon-lined screw cap. The mixture was heated at 120°C for 14 days resulting in pale yellow crystals. The crystals were washed with fresh DMF (×6), methanol (×5) and dried under vacuum to yield the dried sample **1-dried** (14 mg, 59%). Anal. Calc. for C<sub>68</sub>H<sub>40</sub>N<sub>8</sub>O<sub>17</sub>Cu<sub>2</sub>Zn<sub>4</sub> · 3H<sub>2</sub>O: C, 48.51; H, 2.75; N, 6.65. Found: C, 48.29; H, 2.62; N, 6.60%.  $\nu_{\max}$ (neat, cm<sup>-1</sup>): 1606 (s, C=O), 1555 (m, C=C), 1511 (w, C=C), 1377 (s).



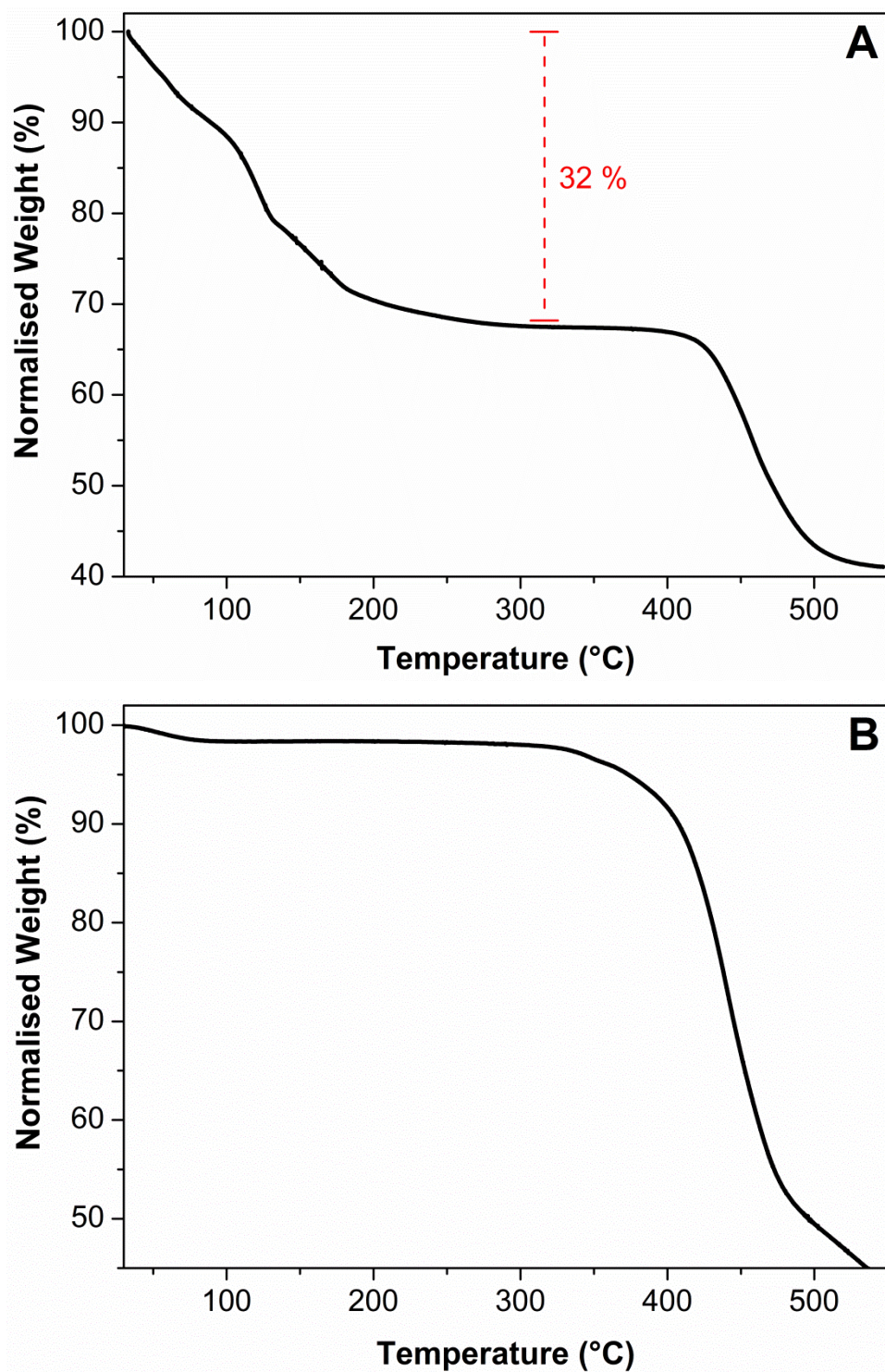
**Figure S1.** PXRD patterns of  $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$  (**1**): a) simulated from the single crystal data, b) in DMF, c) in DCM (which shows both **1** and **1-dried**), and d) in THF.



**Figure S2.** PXRD patterns of  $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$  (**1**): a) simulated from the single crystal data, b) as-synthesized, c) dried, and d) resoluted in DMF.



### 3. Thermogravimetric Analysis



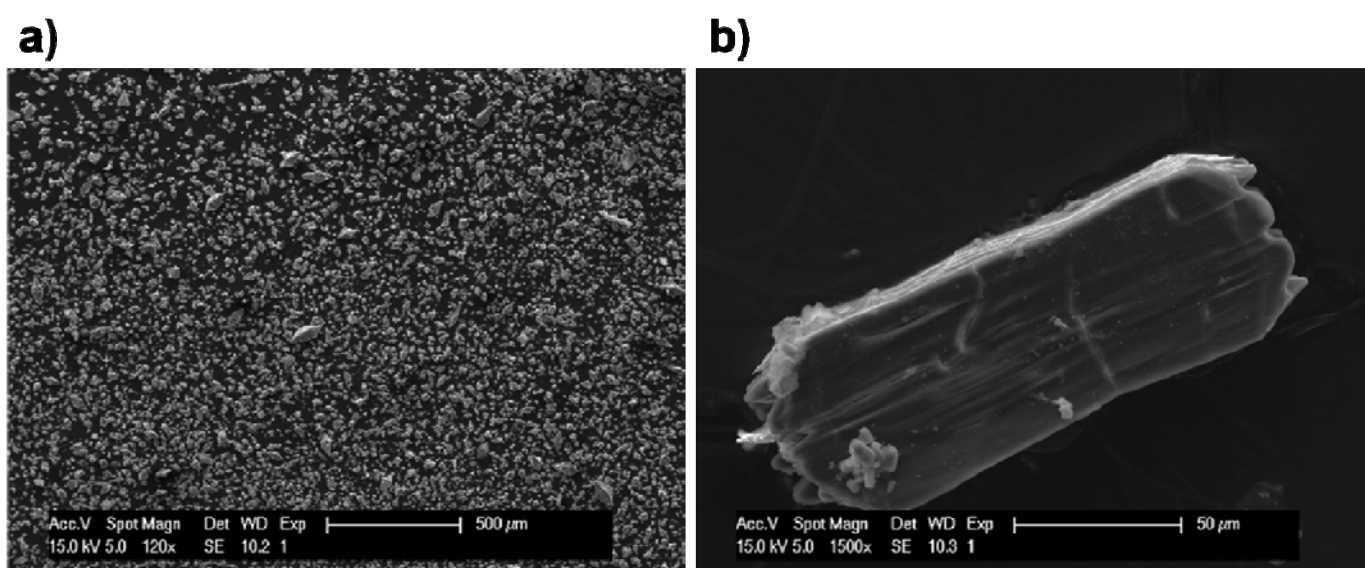
**Figure S3. A.** TGA trace of an as-synthesized sample of **1**. The weight loss of 32% corresponds to solvent molecules lost from the pores of the material. The MOF is thermally stable up to ~400°C. **B.** TGA trace **1-dried**.

#### 4. Energy Dispersive X-ray spectroscopy (EDX)

**Table S1.** Atomic ratio of Zn and Cu in **1** determined by EDX.

Atomic ratio	Cu	Zn
MOF <b>1</b>	0.53	1.00

EDX results are calculated as an average of four areas of a sample (3 mm<sup>2</sup> of crystalline sample). Atomic ratio are normalised to Zn content.



**Figure S4.** SEM images of **1**. (a) An example of an area of crystals used for analysis. (b) An example of a single crystal.

## 5. X-Ray Crystallography

A crystal of **1** was mounted on a plastic loop using paratone-N oil and X-ray diffraction data collected with Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) on an Oxford Diffraction X-calibur diffractometer at 110(2) K. The data set was corrected for absorption and the structures were solved by direct methods using SHELXS-97<sup>3</sup> and refined by full-matrix least squares on  $F^2$  by SHELXL-97,<sup>4</sup> interfaced through the program X-Seed.<sup>5</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise in additional details below. Details of data collections and structure refinements are given in Table S2.

Refinement special details for **1**: The structure of this MOF possesses large voids containing a considerable number of diffuse electron density peaks that could not be adequately modelled as solvent. The SQUEEZE routine of PLATON<sup>6</sup> was applied to the collected data, which resulted in significant reductions in  $R_1$  and  $wR_2$ .  $R_1$  and  $wR_2$  before SQUEEZE routine: 19.93%, 51.4%; after SQUEEZE routine: 12.37%, 37.60%.

**Table S2.** X-ray experimental data for **1**.

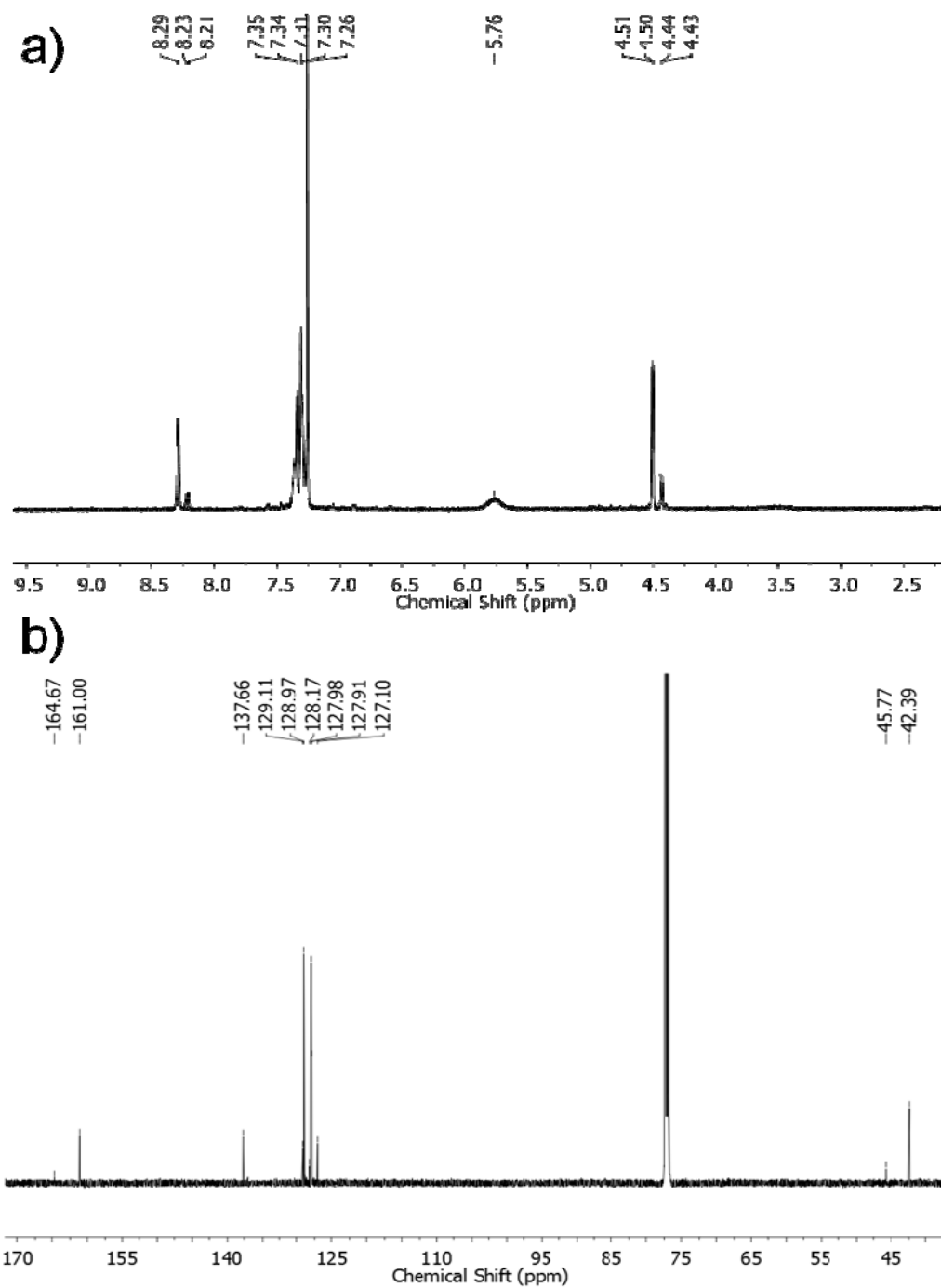
Empirical formula	C <sub>68</sub> H <sub>40</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>17</sub> Zn <sub>4</sub>
Formula weight	1627.62
Crystal system	Orthorhombic
Space group	<i>Ibca</i>
<i>a</i> (Å)	28.1305(9)
<i>b</i> (Å)	26.1877(8)
<i>c</i> (Å)	28.1745(17)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	20755.4(16)
<i>Z</i>	8
Density (calc.) (Mg/m <sup>3</sup> )	1.042
Absorption coefficient (mm <sup>-1</sup> )	1.361
F(000)	6528
Crystal size (mm <sup>3</sup> )	0.20 x 0.18 x 0.09
$\theta$ range for data collection (°)	2.57 - 29.17
Reflections collected	12711
Observed reflections [R(int)]	6666 [0.1060]
Goodness-of-fit on F <sup>2</sup>	1.143
R <sub>1</sub> [I > 2 $\sigma$ (I)]	0.1237
wR <sub>2</sub> (all data)	0.3760
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.455 and -1.372

## 6. Catalysis

### General procedure for Table 1, Entry 3 and Table S3.

MOF **1** (14 mg, 0.0086 mmol, 2.5 mol %) soaked in THF (1.2 mL) was charged in a 50 mL Schlenk under argon. CO<sub>2</sub> (~ 1atm) was then introduced using a balloon by purging the system (×4). Pinacol borane (50 μL, 0.344 mmol) was added dropwise to the solution and the resulting mixture was stirred for 24 h at 35°C. **1** was then removed from the reaction mixture by filtration and NEt<sub>3</sub> (36 μL, 0.258 mmol) and benzylamine (19 μL, 0.172 mmol) were added to the solution under argon. After stirring for 48 h at 65°C, the resulting mixture was directly passed through a pad of silica gel eluting with ethyl acetate. The solvent was then evaporated under vacuum and the residue was directly analysed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>.

Spectroscopic data for *N*-formyl benzylamine were consistent with the previously reported data for this compound.<sup>7</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.29 (s, 0.8H), 8.22 (d, *J* = 12 Hz, 0.2H), 7.30 (m, 5H), 5.76 (s(br), 1H), 4.50 (d, *J* = 6 Hz, 1.6H), 4.43 (d, *J* = 6 Hz, 0.4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 164.7, 161.0, 137.7, 129.1, 129.0, 128.2, 128.0, 127.9, 127.1, 45.8, 42.4. HRMS *m/z*: found 136.0764 [M + H]<sup>+</sup>, calcd 136.0762 for C<sub>8</sub>H<sub>9</sub>NO.

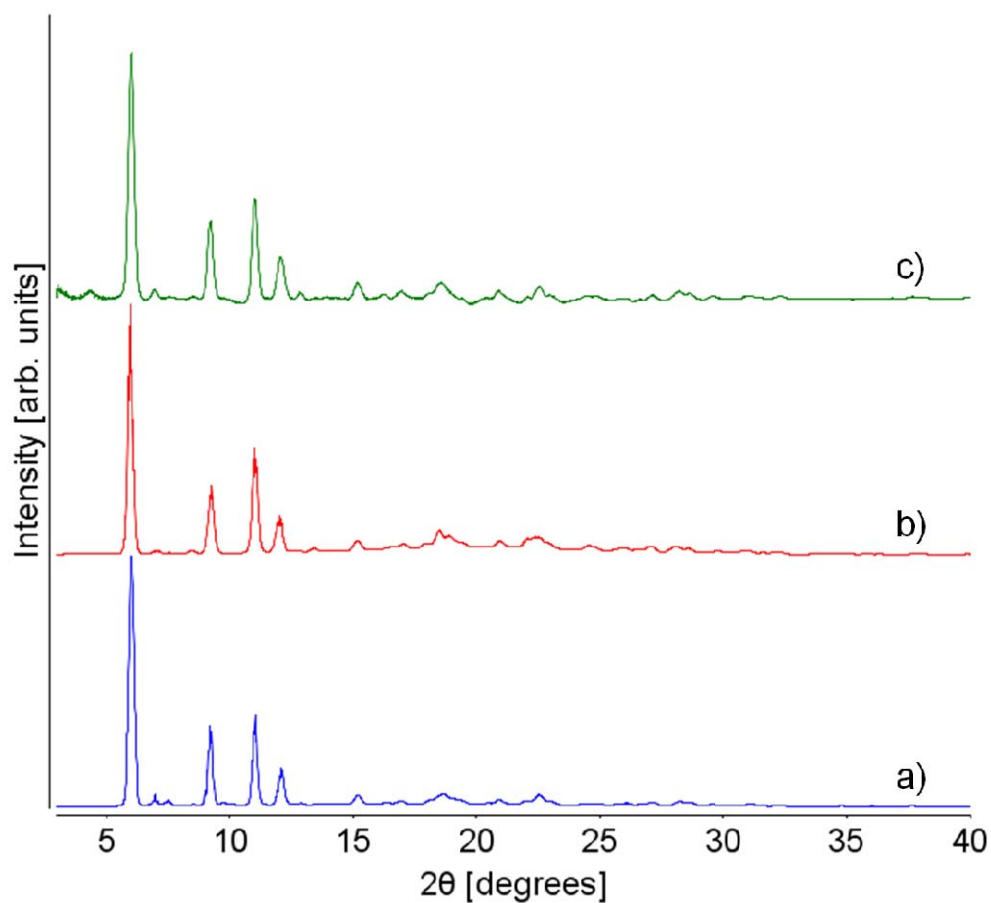


**Figure S5.** a)  $^1\text{H}$  NMR spectrum of *N*-formyl benzylamine. b)  $^{13}\text{C}$  NMR spectrum of *N*-formyl benzylamine.

**Table S3.** Recyclability tests for **1** using 5 mol % loading.

Cycle	1	2	3	4	5
conv. (%) <sup>a</sup>	92	62	53	52	51

<sup>a</sup> Determined by  $^1\text{H}$  NMR spectroscopy.



**Figure S6.** PXRD patterns of **1**: a) as-synthesised, b) after 1<sup>st</sup> catalytic cycle, and c) after 5<sup>th</sup> catalytic cycle.

**Table S4.** Cu concentration in the reaction mixture as measured by ICP-MS after one catalytic cycle.

mol % Cu <sup>a</sup>	Conc. Cu [ppb]	% Cu leached
5	50±2	0.023%

<sup>a</sup> 1 mol % Cu = 0.5 mol % MOF.

## 7. References

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