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ARTICLE TYPE

# Control of Framework Interpenetration for *in situ* Modified Hydroxyl Functionalised IRMOFs

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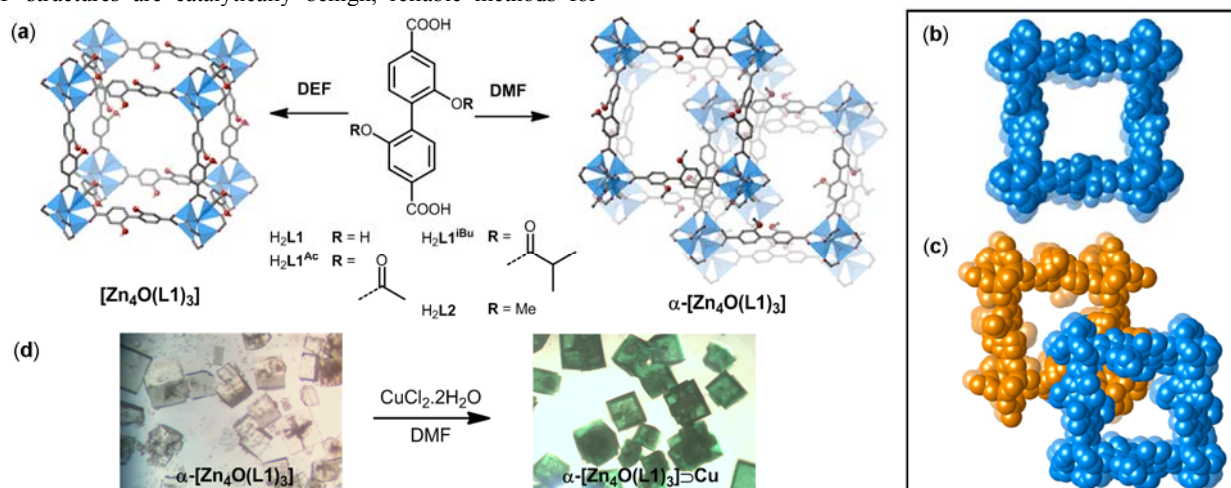
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By intimate control of reaction conditions, phase-pure crystalline porous metal-organic framework materials [Zn<sub>4</sub>O(L)<sub>3</sub>] with interpenetrated and non-interpenetrated structures can be synthesised. Under certain conditions, these reactions occur with concomitant deprotection of masked alcohols located on the organic links which yield accessible ‘metal-binding’ functional groups within the frameworks.

Metal-organic frameworks (MOFs) are constructed by a modular synthetic approach whereby organic links and metal clusters are assembled into porous extended networks via ‘one-pot’ reactions.<sup>1</sup> This has led to the development of design principles that yield precise control of pore dimensions and functionality by utilizing links of identical connectivity but different lengths or non-structural functional groups.<sup>2</sup> Due to their high surface areas, tuneable structure metrics and chemically mutable organic building blocks, MOFs have been identified as materials with great potential for gas separations<sup>3</sup> and size-selective heterogeneous catalysis.<sup>4</sup> To fully realise their catalytic potential MOFs with pores sufficiently large enough to simultaneously allow anchoring of catalytic moieties and diffusion of chemical reactants into the framework is requisite. Furthermore, given that the majority of the metal clusters that comprise the ‘joints’ of MOF structures are catalytically benign, reliable methods for

anchoring catalytic moieties to the framework need to be established. Two major challenges arise; 1) Increasing the pore sizes of topologically identical MOFs commonly affords interpenetration<sup>5</sup> and, 2) utilizing organic links which bear metal-coordinating groups can lead to unwanted side reactions or hinder the formation of the desired networks. Thus, frameworks directly synthesized with free metal-coordinating groups are rare.<sup>6-8</sup>

Recently, post-synthetic modification (PSM) has been developed as a strategy to overcome these challenges and yield open framework materials imbued with novel functionality.<sup>8</sup> A potential drawback of the PSM method is that performing multiple reactions on the MOF crystals can lead to structural decomposition and/or diminished surface area.<sup>9</sup> Thus, to ensure the MOFs retain optimal porosity and crystallinity it is preferable that the most efficient synthetic procedure is employed. Here we report the controlled one-pot synthesis and *in situ* ester hydrolysis of non-interpenetrated and interpenetrated MOFs, [Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>], comprised of biphenyl-2,2’-diol links (L1) (Scheme 1(a)). Notably, both materials can be synthesized in a single-step procedure. It is also noteworthy that the metal coordinating groups are freely accessible in both forms which we demonstrate by the complexation of copper ions and enhanced enthalpy of adsorption for α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] over IRMOF-1.



**Scheme 1.** (a) Synthesis of [Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]. Inset: Space-filling representations of the pores in (b) [Zn<sub>4</sub>O(L1)<sub>3</sub>] and (c) α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]. (d) Images from the metallation studies to generate α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]Cu and show accessibility of the hydroxyl groups.

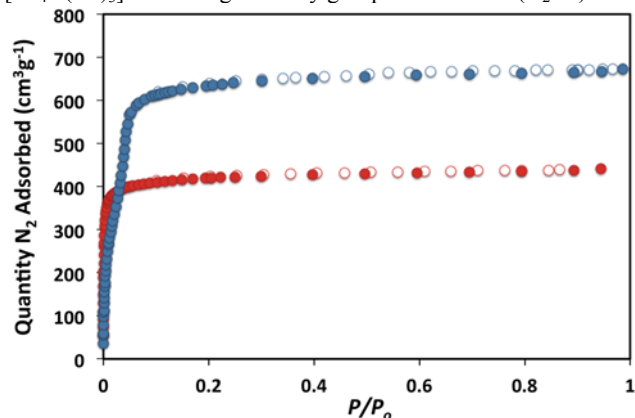
[Zn<sub>4</sub>O(L1)<sub>3</sub>] was synthesized by dissolving 30 mg of H<sub>2</sub>L1<sup>Ac</sup> and 85 mg of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (4 eq) in *N,N'*-diethylformamide (DEF) (4.5 mL) in a tightly-capped 20 mL glass vial.<sup>†</sup> An aliquot of 2.5 M aqueous NaOH solution (30 μL) was then added and the solution heated at 90°C for 20 mins. The solution was then transferred to a new 20 mL vial and heated at 100°C for 36 hours yielding transparent pale yellow, cubic crystals of [Zn<sub>4</sub>O(L1)<sub>3</sub>] with an empirical formula of (C<sub>42</sub>H<sub>24</sub>O<sub>19</sub>Zn<sub>4</sub>). Other more bulky ester protected links (H<sub>2</sub>L1<sup>iBu</sup>) also generated the same non-interpenetrated material. The structure of [Zn<sub>4</sub>O(L1)<sub>3</sub>] was determined by single crystal X-ray diffraction. As anticipated, the framework of [Zn<sub>4</sub>O(L1)<sub>3</sub>] is of cubic topology with Zn<sub>4</sub>O clusters positioned at each of the vertices and biphenyl moieties forming the organic backbone (Scheme 1). The formation of a non-interpenetrated 3-D network is noteworthy given the size of the pore channels (15.4 Å), and the lack of significant steric congestion within the pores arising from the linker.

To ensure that the single crystal structure was representative of the bulk material, samples of [Zn<sub>4</sub>O(L1)<sub>3</sub>] were examined by powder X-ray diffraction (PXRD, Fig. S3).<sup>†</sup> The resultant peak patterns were consistent with that expected for a non-interpenetrated framework. A further noteworthy feature of [Zn<sub>4</sub>O(L1)<sub>3</sub>] is that the acetyl protecting groups are hydrolysed during the one-pot synthesis to afford pores decorated with accessible hydroxyl functional groups. <sup>1</sup>H NMR spectra of digested [Zn<sub>4</sub>O(L1)<sub>3</sub>] reveals all links have been fully deprotected during the course of the reaction. Examples of permanently porous MOFs synthesized from alcohol functionalized links are uncommon,<sup>7, 8</sup> as the free oxygen atoms can participate in metal coordination.<sup>10</sup> For example, we could not form a characterisable MOF from only deprotected ligand (H<sub>2</sub>L1) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, although MOFs with different topologies could be formed with other metals or by incorporating other links. The choice of reaction conditions is also critically important to the nature of the product. Using an analogous procedure, but with DMF as the solvent, we obtained phase-pure interpenetrated α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] from both H<sub>2</sub>L1<sup>Ac</sup> and more sterically-demanding H<sub>2</sub>L1<sup>iBu</sup>. Unit cell determinations for α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] indicated that in this case the framework is two-fold interpenetrated. In addition, the PXRD pattern obtained from bulk samples of α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] closely matched that of the calculated peak positions and intensities for a lower-symmetry two-fold interpenetrated framework.

To determine the permanent porosity of [Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] 77 K N<sub>2</sub> isotherms were carried out on the respective evacuated frameworks (Fig. 1). Based on their isotherms, the BET surface areas of each material were calculated to be 2631 and 1790 m<sup>2</sup>/g<sup>-1</sup> for [Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>], respectively. The isotherm of α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] is best described as Type I, which is indicative of microporosity. A step in the isotherm of [Zn<sub>4</sub>O(L1)<sub>3</sub>] is observed in the low pressure region between P/P<sub>0</sub> of 0.020 and 0.045 and can be attributed to the larger pore volume expected for the non-interpenetrated framework (Scheme 1(b) and (c)).<sup>11</sup> Notably, the synthetic procedure and activation conditions utilized in the present work yielded a surface area for [Zn<sub>4</sub>O(L1)<sub>3</sub>] that is the highest reported for a material based on an IRMOF-9 framework. Thermogravimetric analyses indicate [Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] are thermally stable to 600 and 720 K respectively.<sup>†</sup>

To demonstrate accessibility of the diol chelating sites,

[Zn<sub>4</sub>O(L1)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] were treated with 0.05 M solutions of CuCl<sub>2</sub>·2H<sub>2</sub>O (Scheme 1(d)). Within minutes, crystalline samples of both materials took on a green colour associated with complexation of copper ions by the links. The rate of complexation is consistent with binding to the free diol links rather than incorporation into the metal-oxide nodes of the framework.<sup>12</sup> This colour was retained upon washing. Ester protected [Zn<sub>4</sub>O(L1<sup>Ac</sup>)<sub>3</sub>] and α-[Zn<sub>4</sub>O(L1<sup>Ac</sup>)<sub>3</sub>], synthesised by the same methods for the hydrolysed MOFs but without the addition of base, absorbed copper(II) ions although these could be readily removed by washing. Similar behaviour was also observed for α-[Zn<sub>4</sub>O(L2)<sub>3</sub>] containing methoxy groups on the links (H<sub>2</sub>L2).

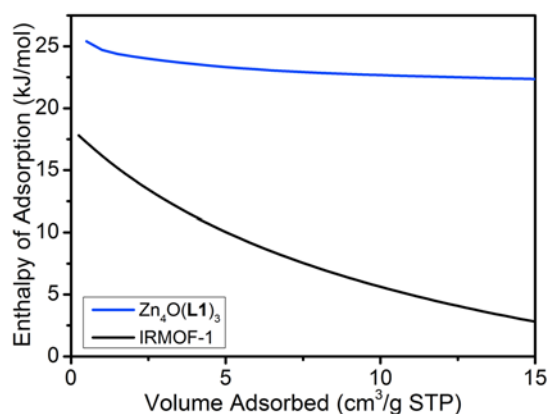


**Figure 1.** N<sub>2</sub> adsorption isotherms at 77 K for [Zn<sub>4</sub>O(L1)<sub>3</sub>] (blue), and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>] (red). Filled and open circles represent adsorption and desorption points, respectively.

The copper(II)-metallated forms, [Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu, were analysed by Energy Dispersive Spectroscopy (EDS). EDS confirmed the loading of Cu in [Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu to have Cu:Zn ratios of ~1:5 and ~1:4 (~27% and ~33% of diol sites), respectively. EDS analysis also revealed that both materials contained no chloride and TGA-FTIR indicated that DMF, potentially within the coordination sphere of the Cu ions, was lost at high temperatures. [Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu and α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu are still permanently porous with BET surface areas of 1675 and 851 m<sup>2</sup>/g<sup>-1</sup>, respectively (Fig. S13). These reductions in surface area are also consistent with in-channel complexation of the copper species. Further evidence for in-channel copper incorporation was provided by a decrease in the pore size distributions for α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]@Cu compared to α-[Zn<sub>4</sub>O(L1)<sub>3</sub>].<sup>†</sup>

To further determine diol accessibility, the effect of hydroxyl groups on CO<sub>2</sub> adsorption was determined by collecting CO<sub>2</sub> isotherms at 273 and 298 K on α-[Zn<sub>4</sub>O(L1)<sub>3</sub>]. It is noteworthy that the polar hydroxyl groups significantly increase the enthalpy of adsorption for CO<sub>2</sub> across the entire coverage range with respect to non-functionalised IRMOF-1 (Fig. 2).<sup>13</sup> This dramatic increase demonstrates that the polar hydroxyl groups are accessible to adsorbates and is due to the surface chemistry given the similarity in pore sizes of the respective materials.

A one-pot synthesis of a non-interpenetrated 3D pillared MOF with organic links bearing non-coordinating hydroxyl groups has been previously reported.<sup>14</sup> In that case, the authors suggest that framework interpenetration was suppressed by the steric bulk of the protecting groups. Similar observations on the control of interpenetration in the IRMOF series have been made.<sup>15,16</sup> Herein however we observe that protecting groups of the same size



**Figure 2.** CO<sub>2</sub> enthalpy of adsorption for  $\alpha$ -[Zn<sub>4</sub>O(L1)<sub>3</sub>], and IRMOF-1.<sup>13</sup>

controllably yield non-interpenetrated and interpenetrated materials but in different solvents. This led us to propose that the hydrolysis rate in the different solvents had a critical role in control of interpenetration; specifically, reactions in DMF led to faster hydrolysis and an interpenetrated product. Monitoring the rate of hydrolysis of the ester protecting group for framework synthesis reactions using H<sub>2</sub>L1<sup>Ac</sup> in DMF and DEF revealed this was not the case (Fig. S7). In fact, crystal growth (6-8 hrs) proceeds considerably faster than link deprotection (up to 36 hrs) indicating the links are deprotected within the framework. While Kim and co-workers have demonstrated that MOF topology is sensitive to small changes in the reaction pH,<sup>17</sup> we can rule out this effect for the diol systems as both [Zn<sub>4</sub>O(L1)<sub>3</sub>] and  $\alpha$ -[Zn<sub>4</sub>O(L1)<sub>3</sub>] can be synthesised in the presence of base and acid. Also in contrast to previous work,<sup>2a, 18</sup> the reactions give phase pure products independent of concentration. Thus, these observations, coupled with the fact that H<sub>2</sub>L1<sup>Ac</sup> and H<sub>2</sub>L1<sup>IBu</sup> form both types of frameworks, point to steric effects deriving from both the link and the solvent having a role in the control of interpenetration. Recently, solvent-mediated control of interpenetration has been observed for other MOF systems.<sup>19</sup>

This work describes the controlled ‘one-pot’ syntheses of MOF materials with two different pore structures bearing accessible alcohol functional groups. Our studies show that suppression of framework interpenetration and control of pore architectures is not only the result of simple steric arguments for the ligand but points toward other mechanisms such as solvent ‘templating’. These findings elucidate novel methodology for synthesizing alcohol functionalized MOFs with controlled pore sizes whereby high molecular weight solvents may be used to control interpenetration. We are currently exploring masking group strategies and solvent combinations to facilitate simultaneous control of pore chemistry and interpenetration in MOFs constructed from longer organic links.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis of H<sub>2</sub>L1, H<sub>2</sub>L1<sup>Ac</sup>, H<sub>2</sub>L1<sup>IBu</sup>, and H<sub>2</sub>L2; synthetic details and activation conditions for the MOFs; <sup>1</sup>H NMR digestion studies; TGA and EDS data; and crystal data and refinement details for [Zn<sub>4</sub>O(L1)<sub>3</sub>] and  $\alpha$ -[Zn<sub>4</sub>O(L2)<sub>3</sub>]. See DOI: 10.1039/b000000x/.

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