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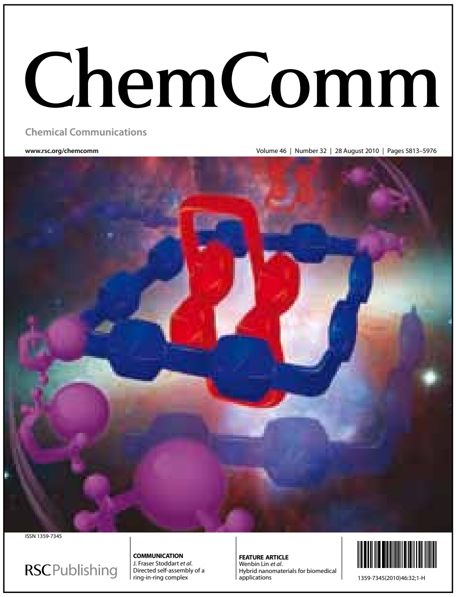

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A reagentless thermal post-synthetic rearrangement of an allyloxy-tagged metal-organic framework

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Direct heating of a metal-organic framework provides a simple, controllable way of effecting a covalent post-synthetic modification. Herein we report that an allyloxy-tagged zinc metal-organic framework undergoes a thermally-promoted aromatic Claisen rearrangement through which the framework connectivity and porosity are maintained.

Metal-organic frameworks (MOFs) are porous solids constructed from component bridging ligands and metal ions that assemble into crystalline lattices.[1] With tuneable pore metrics and chemical functionality, MOFs provide unique environments and opportunities for synthetic chemistry. The main thrust in this area is using MOFs as heterogeneous catalysts wherein they may convey advantages of substrate size selectivity and catalyst recovery for chemical processes.[2] The use of MOFs in stoichiometric or sub-stoichiometric chemical transformations is also possible. In this light, MOFs might be designed so that unusual or novel reactivity is accessed to give products of high value, while retaining the ability to recover and reuse the MOF. Examples demonstrating this kind of reactivity have come from the Fujita group.[3]

A particularly intriguing use of porous MOFs is their potential to act as solid state reaction matrices. This is where the framework backbone acts to hold chemical groups rigidly in place and spatially separate them. Champness, and George and co-workers, for example, used the spatial separation afforded by a framework and immobilised rhenium complexes to enable photo-physical studies.[4] The advantage of immobilisation for avoiding bimolecular catalyst deactivation are recognised in MOF chemistry.[5] Complexed MOF ligands can be viewed as being in a protected form and, by virtue of their incorporation into a framework, chemistry that would otherwise not be possible might be enabled. Reactions on immobilised ligands in a preformed network is, of course, covalent post-synthetic modification (PSM).[6]

MOFs have considerable thermal stabilities, often to several hundred degrees Celsius. Perhaps inevitably, the thermal stabilities of MOFs are drawn in comparison to other porous solid state materials, such as zeolites, which are stable to very high temperatures. As a consequence, MOFs are considered to have only ‘moderate’ thermal stabilities. However, temperatures of up to 350 °C give access to many thermal organic transformations. Thermally-promoted post-synthetic chemistry of MOFs has seen few reports. Telfer has pioneered thermolytic post-synthetic deprotection (PSD) chemistry through the instability of *tert*-butoxycarbamates to unveil amine groups in MOFs, with the additional benefit of concomitant pore enlargement.[7] Very recently, Vittal[8] found that direct heating could dismember cyclobutane rings via a reverse [2+2] cycloaddition process. We sought to explore thermal post-synthetic rearrangement (PSR) chemistry in MOFs as a simple and efficient way of bringing out new functionality in these materials. We rationalised that all atoms required for rearrangements could be installed at the point of MOF formation through a direct synthesis and this would completely eliminate the need for chemical reagents in the post-synthetic step. All that is required to bring about the MOF modification is just to heat it.

It is now 100 years since Claisen[9] reported the thermal rearrangement of allylphenyl ethers to *ortho*-allyl phenols – the aromatic Claisen rearrangement. This celebrated reaction is now the textbook example of sigmatropic rearrangements. The aromatic Claisen rearrangement has many successful reaction variants and yet, the classic conditions of heating in a high boiling solvent remains in high use.[10] In this communication we report on the first example of thermally-promoted PSR chemistry in a porous MOF through direct heating of the solid.

We prepared 2-(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylic acid $H_2\mathbf{L}^1$† as a ligand with a linear biphenyl dicarboxylic acid backbone and a pendant allyloxy tag group (Fig. 1) that would allow us to target a cubic structure based on the well-known zinc IRMOF series.[11] The tag group was positioned on the ligand backbone to project into the pore space of the resultant MOF where it could attain the conformation needed to undergo the rearrangement.

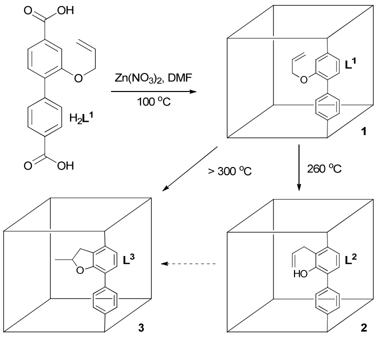

Fig 1 The structure of $H_2\mathbf{L}^1$ and synthetic conditions to form **1-3**. One network and the major ligand component of each PSR is shown.

$H_2\mathbf{L}^1$ was reacted with $Zn(NO_3)_2{\cdot}6H_2O$ in hot DMF‡ to give slightly opaque cubic crystals of **1** that were analysed by single crystal X-ray diffraction. **1** crystallises in the space group *C*2/*m* with similar unit cell parameters to those we have observed for zinc MOFs with aldehyde-, sulfide- and sulfone-tagged biphenyl dicarboxylate ligands.[12] The structure exists as a pair of interpenetrating cubic networks (Fig. 2), separated by *ca.* 4–5 Å between phenyl rings of the linkers, and with a framework formula of $[Zn_4O(\mathbf{L}^1)_3(DMF)_2]$. One of the zinc centres coordinates 2 DMF ligands and adopts a distorted octahedral geometry. The Zn_4O SBU falls across the mirror plane of the space group as does a bridging ligand and this contributes to rotational disorder of the linker. Remarkably, despite this disorder, the first three atoms of the pendant allyloxy tag stemming from this ligands backbone could be located crystallographically. Typically, the positions of the atoms of tag groups are not observed due to disorder. The terminal carbon atom of the allyloxy group could not be reliably located in the final difference Fourier electron density map, but this is not surprising given the disorder present. However, through digestion and solution ^1H NMR analysis of **1** it was confirmed that $\mathbf{L}^1$ was unchanged upon incorporation into the MOF.

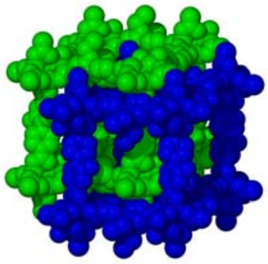

Fig. 2 The doubly interpenetrated structure of **1**.

Following solvent exchange and vacuum drying,‡ powdered **1** was analysed by simultaneous thermogravimetric–differential thermal analysis (TG–DTA) under an atmosphere of nitrogen gas (Fig. 3). The TG curve shows a mass loss of 3.5% between room temperature and 100 ºC, corresponding to some residual solvent being driven from the framework, before a broad plateau of stability to around 380 ºC, whereupon the onset of decomposition occurs. In the DTA curve the endothermic solvent loss is followed by a prominent exotherm which is observed to occur with no concurrent mass loss. This is consistent with the process of a rearrangement taking place where no atoms are lost or gained.

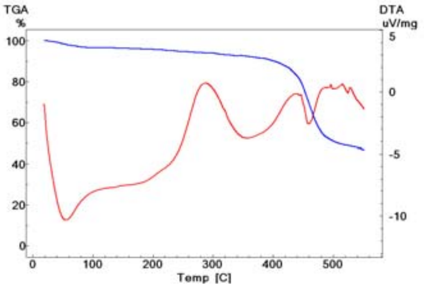

Fig. 3 TG—DTA curves for heating dried **1** to 550 °C. The blue curve shows the TG response. The red curve shows the DTA response.

The heating protocol was modified to hold the sample at 260 ºC† and the PSR product, **2**, was recovered. The ^1H NMR spectra of the recovered material† showed the presence of unreacted $H_2\mathbf{L}^1$, the desired PSR product $H_2\mathbf{L}^2$, and a product containing a furan ring, $H_2\mathbf{L}^3$ (Fig. 1). The optimum conditions for the generation of $H_2\mathbf{L}^2$ required a hold time of 20 minutes, which typically gave a ratio of $H_2\mathbf{L}^1$: $H_2\mathbf{L}^2$: $H_2\mathbf{L}^3$ of 1 : 7 : 0.5, respectively, resulting in a formulation for **2** of $[Zn_4O(\mathbf{L}^1)_{0.33}(\mathbf{L}^2)_{2.47}(\mathbf{L}^3)_{0.17}]$. Thus, this modification is efficient with only around 10% of starting allyloxy groups remaining. The rearrangement temperature of 260 ºC was definitively established as when the material was heated to 250 ºC, analysis of the the material through digestion and solution ^1H NMR spectroscopy, showed only $H_2\mathbf{L}^1$.

To examine the crystallinity of the frameworks, **1** and **2** were analysed by powder X-ray diffraction (PXRD) (Fig. 4). The excellent correspondence of peaks between the samples indicates the connectivity of the framework has not changed as a result of the PSR.

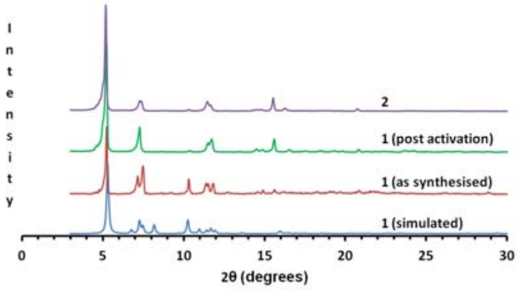

Fig. 4 PXRD patterns for **1** and **2**.

Direct evidence that porosity is retained during the rearrangement from **1** to **2** comes from nitrogen gas adsorption measurements at 77 K (Fig. 5). After activation at 145 ºC, **1** shows a Type I isotherm that gives a Brunauer-Emmett-Teller (BET) surface area of 1348 $m^2\ g^{-1}$ (Langmuir, 1464 $m^2\ g^{-1}$). The sample was retained in the instrument and heated to 260 ºC and the BET surface area was found to be 1360 $m^2\ g^{-1}$ (Langmuir, 1477 $m^2\ g^{-1}$) with a near identical isotherm. ^1H NMR analysis following digestion showed that the composition of the MOF material from this experiment was $[Zn_4O(\mathbf{L}^1)_{0.26}(\mathbf{L}^2)_{1.96}(\mathbf{L}^3)_{0.78}]$.

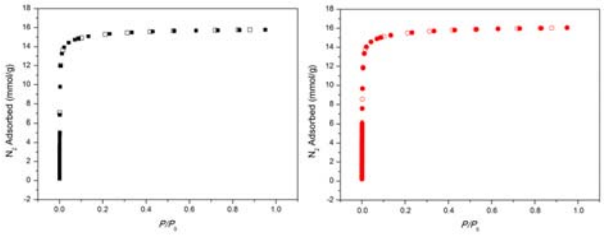

Fig. 5 Nitrogen gas adsorption/desorption isotherms for the in situ conversion of **1** (left) to **2** (right). Closed squares/circles adsorption, open squares/circles desorption.

When $H_2\mathbf{L}^2$ was used as a ligand in MOF synthesis under the same reaction conditions used for $H_2\mathbf{L}^1$ there was no formation of any solid product. This result indicates that post-synthetic modification provides the best, and, perhaps, the only way to prepare **2**. We also tried to prepare a zinc MOF from 2-hydroxy-

[1,1'-biphenyl]-4,4'-dicarboxylic acid in DMF solution and found that no solid was produced in this reaction. However, during the course of our study it was reported that when using DEF as the reaction solvent the interpenetrated cubic structure is formed.[13] MOFs with non-coordinated hydroxyl groups are relatively rare[13, 14] but are desirable as groups for tuning the adsorptive performance of MOF materials. Recently a method with seemingly general applicability for hydroxyl functionalised MOFs has appeared.[15]

We became interested in the observation of $\mathbf{L^3}$ within the PSR process. Coordinated $\mathbf{L^3}$ comes from $\mathbf{L^2}$ *via* a cyclisation pathway and longer hold times leads to increased proportions of $\mathbf{L^3}$ at the expense of $\mathbf{L^2}$. Much better results were obtained, however, by employing higher temperatures and we found that by heating to 300 ºC, or above, $\mathbf{L^3}$ becomes the dominant product. Remarkably, crystallinity is still maintained in this process as evidenced by the PXRD patterns.† Thus this sequence is controllable through extending the heating time but shows better response to temperature. The best conversions to $\mathbf{L^3}$ were obtained with a heating rate of 15 °C min^{-1} to 320 °C and a hold time of 20 minutes. This gave a MOF with the formulation of $[Zn_4O(\mathbf{L^2})_{0.45}(\mathbf{L^3})_{2.55}]$ **3** as judged through ^{1}H NMR spectroscopy of the digested product.† At these temperatures some terminal-to-internal alkene isomerisation is observable, but only in very small amounts (<5%). Significantly, this transformation cannot be efficiently carried out by direct heating of $H_2\mathbf{L^1}$ itself, as it undergoes decomposition before these temperatures. Mass spectrometry of the digested samples shows a signal at twice the expected mass, suggesting that not all of the rearrangement processes have complete reticular fidelity and that there are inter-reticular reactions between pairs of ligands close by in the interpenetrated framework. This is an interesting type of reactivity as it results in covalently linking the networks together.

In summary, we have shown that high temperature organic chemistry is accessible in porous MOF systems through direct heating in a controllable way. This method thus provides a potentially valuable addition to the existing methods for covalent PSM in MOFs. Demonstrated here is an example whereby a chemical transformation can be done on the linker because of increased stability *via* framework incarceration. Considering the high temperatures and possible competing reaction pathways, the PSRs described herein occur remarkably cleanly and in high yields. The success of this example has focussed our attention to establishing the generality of thermally-promoted PSRs in MOFs and we are now investigating other examples.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis of $H_2\mathbf{L^1}$, TG–DTA data, PXRD patterns for **1** and **3**; selected single crystal data for **1**; ^{1}H NMR digestion spectra. CCDC 910203. See DOI: 10.1039/b000000x/

‡ *MOF synthesis* $H_2\mathbf{L^1}$ (100 mg, 0.34 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (300 mg, 1.0 mmol) were dissolved in DMF (18 cm^3) and heated in an oven for 24 hours. The crystals were solvent exchanged with fresh portions of anhydrous DMF then with CH_2Cl_2 and finally with benzene. Samples were left under benzene until required whereupon they were freeze dried. A typical yield from this process was 100 mg. Found: C, 49.77; H, 3.07; N. 0.00. $[Zn_4O(\mathbf{L^1})_3]{\cdot}3.5H_2O$ requires C, 49.80; H, 3.51; N, 0.00.

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