Metal–Organic Frameworks

DOI: 10.1002/ange.200802908

Post-Synthetic Modification of Tagged Metal–Organic Frameworks**

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Metal–organic frameworks (MOFs) are currently attracting considerable attention,[1] largely because of their potential for porosity, and their consequent use in applications as diverse as gas storage,[2] catalysis,[3] separations,[4] and drug delivery.[5] The first generation of MOFs were formed by linking together metal centers with simple, commercially available bridging ligands, such as 1,4-benzenedicarboxylate (bdc),[6] but there has since been an increasing shift towards more complex structures and increased functionality. For example, MOFs in which the pores contain accessible hydrogen-bonding groups,[7] unsaturated metal centers,[8] or chirality[9] have been reported and studied, and the preparation of dynamic porous materials, capable of undergoing guest-induced transformations or reformations, has been explored.[10]

Another approach to forming functionalized networks is to undertake reactions on preformed MOFs, converting one solid state material into another. The incorporation of an additional functional group, a "tag", into a linking ligand offers the opportunity to form structures in which this group is preserved during the MOF synthesis, allowing it to project into the pores or channels of the network structure. We define a "tag" as a group or functionality that is stable and innocent (that is, non-structure-defining) during MOF formation, but that can be transformed by a post-synthetic modification. This approach is shown schematically in Figure 1. A similar concept of tagging has also recently been applied in medicinal chemistry.[11]

Post-synthetic modification allows the pores in a preformed MOF to be tailored for a specific purpose, which offers the possibility of fine-tuning for selective adsorption and catalysis. The strategy also facilitates the incorporation into a MOF of functional groups that would not survive the conditions of the MOF synthesis (e.g., temperature and pH) and of functional groups that might compete with the donor groups on the bridging ligands. Given these advantages, it is surprising that there has been very little focus on post-synthetic modification of MOFs.[12] Kim and co-workers showed that the pendant pyridyl groups in a chiral zinc network could be methylated[13] and, very recently, Wang and Cohen,[14] and Gamez and co-workers[15] have both demonstrated that the amino groups in 2-amino-1,4-benzenedicarboxylate MOFs can be converted into amides or urethanes. Rosseinsky and co-workers have converted these amines into salicylidenes, and then used these to coordinate vanadium.[16] Fujita and co-workers have shown that guest molecules can undergo similar transformations within the pores of a MOF.[17]

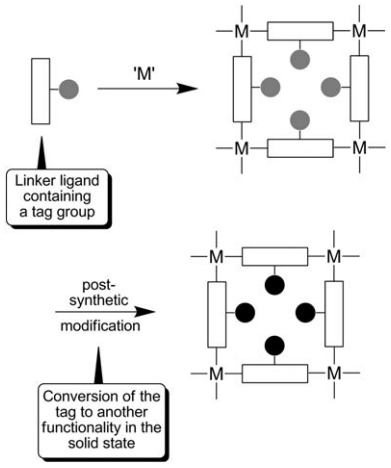
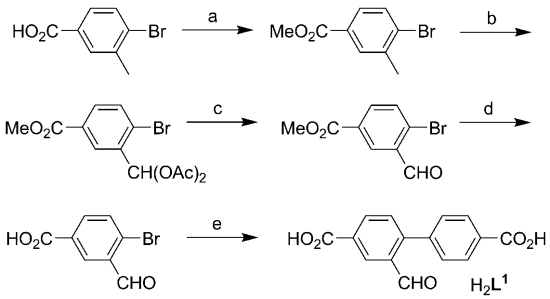


Figure 1. Schematic representation of the post-synthetic modification strategy for MOFs.

Herein, we report our endeavors to prepare tagged MOFs suitable for post-synthetic modification, starting from an aldehyde-modified dicarboxylate. Following seminal work from Yaghi and co-workers, it is now well-established that the octahedral zinc secondary building unit (SBU) $Zn_4O(O_2CR)_6$ forms an isoreticular series of MOFs containing the same framework topology with linear dicarboxylates, such as bdc and 4,4′-biphenyldicarboxylate (bpdc).[6] We have prepared the aldehyde-tagged dicarboxylic acid $H_2\mathbf{L^1}$ (2-formylbiphenyl-4,4′-dicarboxylic acid, Scheme 1), and used it in MOF synthesis. The coordinated $\mathbf{L^1}$ ligand is suitable for



Scheme 1. Preparation of aldehyde-tagged dicarboxylic acid $H_2\mathbf{L^1}$: a) $MeOH/H_2SO_4$; b) $CrO_3/AcOH/Ac_2O$; c) $MeOH/H_2O/H_2SO_4$; d) NaOH/MeOH followed by HCl; e) 4-carboxyphenylboronic acid/$[PdBr_2(dppf)]/Na_2CO_3$/DMF.

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[**] The Leverhulme Trust and the EPSRC are thanked for financial support, and one of the referees is thanked for helpful comments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802908.

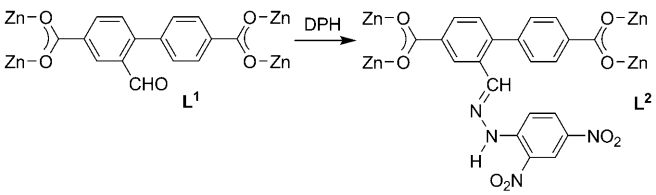
further reaction, and we demonstrate the conversion of $\mathbf{L^1}$ into the 2,4-dinitrophenylhydrazone ligand $\mathbf{L^2}$ within the network structure of the MOF. As a comparison, we also report use of the methoxy-modified dicarboxylic acid $H_2\mathbf{L^3}$ in MOF synthesis, and demonstrate that $\mathbf{L^3}$ is unable to undergo analogous reactions in a MOF.

The reaction between $Zn(NO_3)_2{\cdot}6H_2O$ and $H_2\mathbf{L^1}$ in DMF at 100 °C gave colorless crystals over 24 h, and these were characterized crystallographically as $[Zn_4O(\mathbf{L^1})_3(OH_2)_2]{\cdot}4DMF$ (**1**). The asymmetric unit of **1** contains one full and two half zinc atoms, half an oxygen atom at the center of the SBU, one and a half $\mathbf{L^1}$ ligands, two aqua ligands and some diffuse solvent (taken as DMF). The X-ray analysis confirmed that **1** adopted the doubly-interpenetrated cubic network observed previously for $[Zn_4O(bpdc)_3]$ (IRMOF-9),[6] but significant rotational disorder of the phenyl rings of the ligand, coupled with the positional disorder of the aldehyde group over the *ortho* sites meant that the aldehyde tag could not be reliably observed by crystallography. Two water molecules are coordinated to one of the zinc centers, changing its coordination geometry from tetrahedral to octahedral.

The microanalytical data for **1** are consistent with the network structure, and suggest that both DMF and water molecules remain present in the pores after the material has been heated for 1 h at 100 °C under vacuum. Desolvated samples of **1** retain their integrity, and following immersion of a desolvated sample in DMF for four weeks, a single crystal data collection confirmed the crystal structure had not altered on desolvation/resolvation.

To assess the applicability of **1** to post-synthetic modification, crystals were placed in a DMF solution of 2,4-dinitrophenylhydrazine (DPH) at room temperature. DPH was chosen, as conversion of the formyl group to a hydrazone would be easy to detect through a change in color. The crystals adopted the color of the solution within 2 h and, after a week, the resulting orange-red crystals (**2**) were isolated by filtration, soaked in and washed with DMF to remove any unreacted DPH, then analyzed by microanalysis and X-ray diffraction. The solid lost none of its color on washing, suggesting that the hydrazine had been incorporated into the network as intended. The crystals were cleaved to confirm that the color change penetrated throughout and that reaction had not just occurred on the surfaces. Microanalyses on samples left under DMF solutions of DPH for 1 week and for 4 weeks both suggested that 50 %–60 % of the aldehyde tags had reacted. A sample of **2** was digested in 35 % DCl/D_2O and $[D_6]DMSO$[14] and analyzed by ^1H NMR spectroscopy. The spectrum gave a ratio of aldehyde to hydrazone of 40:60, giving a formulation (without solvent) for the modified network of $[Zn_4O(\mathbf{L^1})_{1.2}(\mathbf{L^2})_{1.8}]$, where $\mathbf{L^2}$ is the 2-[(2,4-dinitrophenyl)hydrazonomethyl]biphenyl-4,4′-dicarboxylate ligand, formed within the MOF network (see Scheme 2). There was no evidence in the ^1H NMR spectrum of free DPH, either as a result of hydrolysis of the hydrazone or inclusion as a guest within the pores.

The IR spectrum of **2** was identical to that of **1** with the exception of two additional peaks, at 1520 and 1328 cm^{-1} which can be attributed to the nitro groups. The X-ray single



Scheme 2. Post-synthetic modification of the formyl group of $\mathbf{L^1}$ (within **1**) to the hydrazone ligand $\mathbf{L^2}$ (within **2**).

crystal analysis of **2** confirmed that the doubly interpenetrated cubic network of **1** was still present, and that aldehyde groups had been converted to hydrazone groups. The asymmetric unit consists of two half-occupancy zinc centers [Zn(1) and Zn(3)], located on a mirror plane, one full-occupancy zinc [Zn(2)], half an oxygen atom, 0.6 $\mathbf{L^1}$ ligands, 0.9 $\mathbf{L^2}$ ligands, two half-occupancy aqua ligands and eight molecules of diffuse solvent (taken as water), giving an overall formula for **2** of $[Zn_4O(\mathbf{L^1})_{1.2}(\mathbf{L^2})_{1.8}(OH_2)_2]{\cdot}16H_2O$.

The SBU of **2** consists of $Zn_4O(O_2CR)_6(OH_2)_2$ units, as shown in Figure 2. Notably, as in **1**, one of the zinc centers,

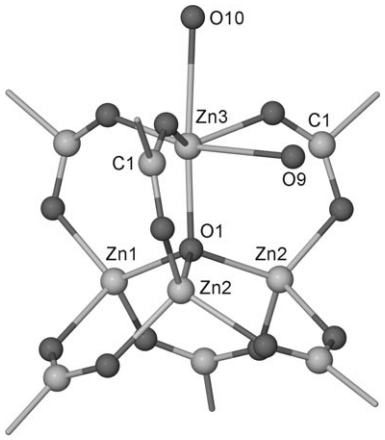


Figure 2. The SBU in the structure of $[Zn_4O(\mathbf{L^1})_{1.2}(\mathbf{L^2})_{1.8}(OH_2)_2]{\cdot}16H_2O$, **2**. Coordination of the two aqua ligands to Zn3 opens up one of the inter-carboxylate angles allowing the modified tag to be incorporated.

Zn(3), is coordinated to two water molecules in addition to the three carboxylate oxygen atoms and the central oxo group, giving rise to a distorted octahedral geometry around Zn(3). This in turn serves to open up the angle between two of the carboxylate groups, which can be quantified by a C(1)-O(1)-C(1)′ angle of 103.4°. This distortion helps to accommodate the modified tag within the pores.

The gross structure of the interpenetrated networks is shown in Figure 3. The aldehyde and hydrazone groups are disordered within the structure so, for each network, three partial occupancy hydrazone-modified tags are directed into every cubic pore. The two interpenetrated networks are closer together in **2** than in IRMOF-9, as evidenced by the shorter Zn···Zn contact (6.92 Å in **2**, compared with 8.09 Å in IRMOF-9).[6] This shift helps to accommodate the hydrazone groups within the pores.

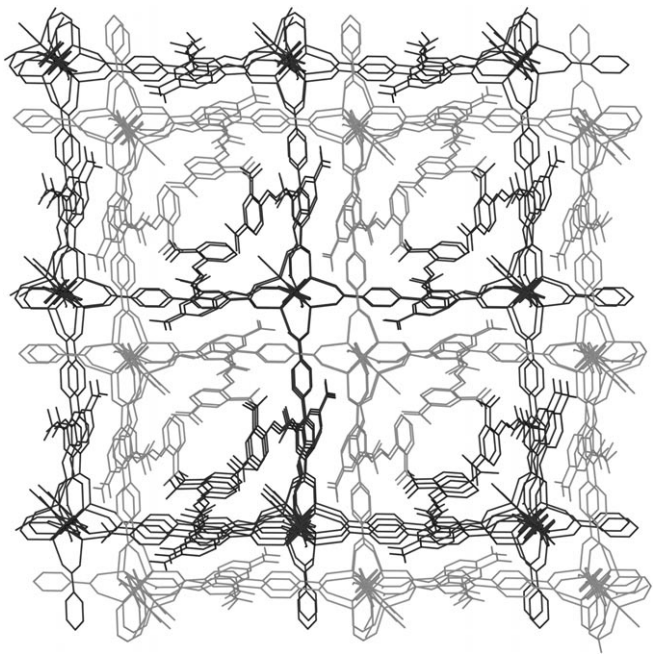
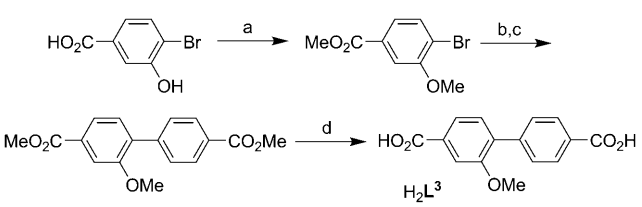


Figure 3. The network structure of $[Zn_4O(\mathbf{L^1})_{1.2}(\mathbf{L^2})_{1.8}(OH_2)_2]\cdot 16H_2O$ **2**, with the two interpenetrated networks shown in different shades. The hydrogen atoms have been omitted for clarity. The hydrazone functionalities exhibit partial occupancy.

Since the reaction of **1** with DPH gives only partial conversion of the aldehyde tags to hydrazone groups, even after four weeks in the presence of excess DPH, it seems that it is not possible to prepare the fully transformed product $[Zn_4O(\mathbf{L^2})_3]$ by post-synthetic modification. To determine whether $[Zn_4O(\mathbf{L^2})_3]$ can be formed directly, $H_2\mathbf{L^1}$ was converted to 2-[(2,4-dinitrophenyl)hydrazonomethyl]-biphenyl-4,4′-dicarboxylic acid, $H_2\mathbf{L^2}$, by reaction with DPH in refluxing dioxane. $H_2\mathbf{L^2}$ was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry. The reaction of $Zn(NO_3)_2\cdot 6H_2O$ with $H_2\mathbf{L^2}$ did not give an analogous product to **1** and **2**, demonstrating that post-synthetic modification allows access to products that differ from those formed by direct reaction between a metal salt and a ligand.

To further understand the conversion of **1** to **2**, an equivalent MOF that is incapable of post-synthetic modification was studied for comparison. 2-Methoxybiphenyl-4,4′-dicarboxylic acid ($H_2\mathbf{L^3}$) was prepared in the three-step process shown in Scheme 3.



Scheme 3. Preparation of $H_2\mathbf{L^3}$: a) MeI/K_2CO_3/DMF; b) 4-carboxyphenylboronic acid/[$PdBr_2$(dppf)]/Na_2CO_3/DMF; c) MeOH/H_2SO_4; d) NaOH/MeOH, followed by HCl.

The methoxy group was chosen since it is similar in size and composition to the formyl tag, but is unable to react with DPH. The reaction between $Zn(NO_3)_2\cdot 6H_2O$ and $H_2\mathbf{L^3}$ in DMF at 100 °C over 24 h, gave colorless crystals. These were characterized (without solvent) as $[Zn_4O(\mathbf{L^3})_3]$ (**3**). X-ray crystallographic analysis of **3** yielded similar unit cell dimensions to those of **1** and **2**, but full structural characterization was hampered by poor diffraction. Crystals of **3** were placed in a DMF solution of DPH and, after 4 weeks, the crystals were isolated by filtration, soaked in portions of fresh DMF, washed with DMF, and then analyzed. Before washing, the crystals were noted to be a paler orange than those of **2**, and this color disappeared on soaking and washing. This suggests that the color was caused by DPH molecules on the surfaces and/or within the pores, confirming that no reaction between DPH and the network had occurred.

Given the similarity in size between $\mathbf{L^1}$ and $\mathbf{L^3}$, we reasoned it might be possible to form a mixed-ligand MOF, incorporating both $\mathbf{L^1}$ and $\mathbf{L^3}$ in the same crystal. Significantly, a mixed-ligand MOF would allow the doping of a small quantity of tags into a MOF, which would in turn facilitate low loadings of the modified functionalities. A restricted number of tags offers a means of avoiding pore blockage on post-synthetic modification, if this problem arises.

The reaction of $Zn(NO_3)_2\cdot 6H_2O$ with a 1:1 ratio of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^3}$ gave a material with the formula $[Zn_4O(\mathbf{L^1})_x(\mathbf{L^3})_{3-x}]$ (**4**). X-ray analysis of **4** yielded similar cell parameters to those for **1**–**3**, but the data were not of sufficient quality to resolve the aldehyde or methoxy groups. To determine the value of x, a sample of **4** was digested in DCl/D_2O and [D_6]DMSO and analyzed by ^{1}H NMR spectroscopy. Perhaps surprisingly, given the ratio of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^3}$ used in the synthesis, the ^{1}H NMR spectrum gave a $H_2\mathbf{L^1}$:$H_2\mathbf{L^3}$ ratio of 10:90, allowing **4** to be formulated (without solvent) as $[Zn_4O(\mathbf{L^1})_{0.3}(\mathbf{L^3})_{2.7}]$.

Compound **4** behaves significantly differently from **1** and **3** on treatment with DPH. On standing under a DMF solution of DPH for a week, DPH is taken up and the color remains in the crystals, in contrast to observations with **3**. The uptake is, however, in much reduced quantities than for **1**, as witnessed by the intensity of the color. To determine the formulation of the DPH-modified network **5**, a sample was digested in DCl/D_2O and [D_6]DMSO and analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed the presence of $H_2\mathbf{L^2}$ and $H_2\mathbf{L^3}$ in a 10:90 ratio, with no evidence for the presence of $H_2\mathbf{L^1}$, suggesting that all of the aldehyde tags in **4** have reacted with DPH to give $[Zn_4O(\mathbf{L^2})_{0.3}(\mathbf{L^3})_{2.7}]$. To confirm that **5** was a mixed-ligand MOF, and not simply a mixture of the homoleptic networks **3** and $[Zn_4O(\mathbf{L^2})_3]$, several crystals were selected and individually digested in HCl (aq). These solutions were diluted with methanol and analyzed by ESI mass spectrometry. In all cases, the negative-ion mass spectra showed peaks for $[H\mathbf{L^3}]^-$ and $[H\mathbf{L^2}]^-$, demonstrating the presence of both ligands within each crystal.

A crystal of **5** was also selected for X-ray crystallographic analysis. The crystal structure is consistent with the formula $[Zn_4O(\mathbf{L^2})_{0.3}(\mathbf{L^3})_{2.7}(DMF)_2]\cdot 3.2H_2O$ **5** (Figure 4). The gross structure of **5** is similar to that of **2**, containing two interpenetrating networks, but there are some fundamental differ-

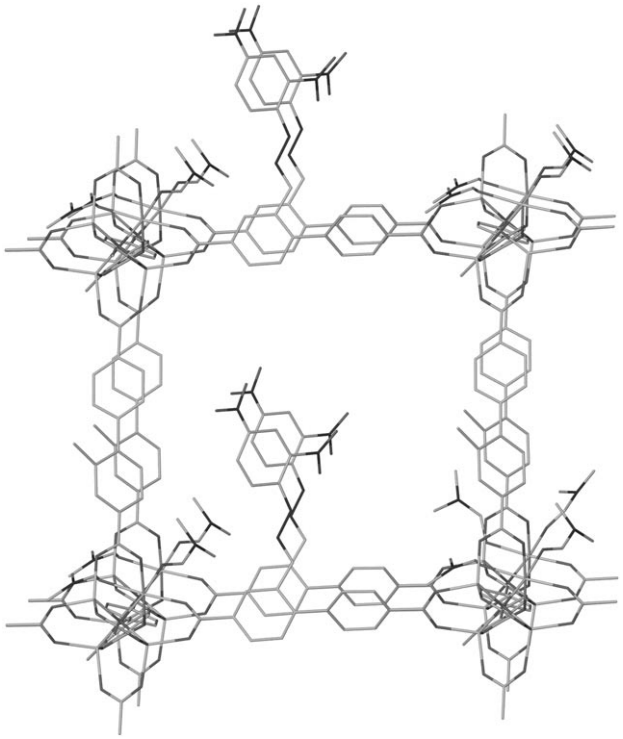


Figure 4. Part of one of the interpenetrated networks in the structure of $[Zn_4O(\mathbf{L^2})_{0.3}(\mathbf{L^3})_{2.7}(DMF)_2]\cdot 3.2\,H_2O$, **5**. Only one position of the disordered hydrazone groups are shown, and hydrogen atoms have been omitted for clarity.

ences. Firstly, the SBU contains two DMF ligands, as opposed to two aqua ligands, on the octahedral metal center. However, the distortion of the SBU is similar to that in **2** with a C-O-C′ angle of 102.0° quantifying the widening of the angle between two of the carboxylates, which helps to accommodate the hydrazone group. The closest Zn···Zn contact between the interpenetrated networks (6.88 Å) is similar to that in **2**.

In conclusion, we have shown that reactive tag groups can be incorporated into the pores of MOFs, and that these are able to undergo post-synthetic modification under mild conditions at room temperature. For the reaction of **1** with DPH to form **2**, this conversion involves a single-crystal-to-single-crystal transformation, affording a product that is not accessible by direct combination of metal salt and ligands. The distance between the dicarboxylic acids in $H_2\mathbf{L^{1-3}}$ is greater than that in H_2bdc, although the size of the pore windows is reduced by interpenetration. From space-filling models of the crystal structures,[6] and assuming no rotation about the C–C bonds, we estimate a pore window width of 8.7 Å for the framework in **2**, which compares with 7.7 Å for $[Zn_4O(bdc)_3]$ (MOF-5) and 7.2 Å for IRMOF-9. The difference in pore-window size between the interpenetrated structures of **2** and IRMOF-9 is due to the relative positions of the two networks within each structure, as noted above. This suggests that the doubly-interpenetrated network in these systems is dynamic,[10] and able to adjust the sizes of the pores and their associated windows to accommodate larger molecules.

By using a combination of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^3}$, we have demonstrated that it is possible to dope tag groups into MOFs, then selectively functionalize these. This result could have important implications for the use of MOFs as catalyst supports, since doping provides a means of controlling the loading of a catalyst in a MOF. In addition, this method may allow the preparation of MOFs containing more than one type of modification in a controlled manner.

Experimental Section

Full experimental details, including the syntheses of $H_2\mathbf{L^1}$, $H_2\mathbf{L^2}$, $H_2\mathbf{L^3}$, and **1**–**5**, and crystallographic data for **1**, **2** and **5** are described in the Supporting Information. CCDC 691966 (**1**), 661967 (**2**), and 691968 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Received: June 18, 2008
Published online: September 29, 2008

Keywords: metal–organic frameworks · microporous materials · post-synthetic modification · X-ray diffraction · zinc

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