Sulfur-tagged metal–organic frameworks and their post-synthetic oxidation†

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A series of sulfur-tagged zinc MOFs containing functionalised 4,4′-biphenyldicarboxylate ligands has been prepared: oxidative post-synthetic modification with dimethyldioxirane has converted the sulfide tags into sulfones, leaving the MOF networks intact.

The first decade of the 21st century has witnessed a vast surge of interest in metal–organic frameworks (MOFs).[1] As MOF chemistry matures, there has been an increasing shift towards more complex structures and increased functionality. This has given rise to problems in both synthesis and characterisation, since pre-functionalised linker ligands may not give the desired network topology, while crystal structures are often plagued with disorder, preventing full structural characterisation. Post-synthetic modification (PSM) has recently emerged as a powerful tool for introducing functionality to MOFs by covalent reactions involving functional groups that project into the pores of pre-formed MOFs.[2] A major advantage of this approach is the ability to incorporate chemical functionality that might not otherwise be possible. The straightforward isolation procedures afforded by heterogeneous functionalisation are also beneficial. Indeed, procedures and techniques developed for, and commonly used with, resins and beads may prove employable in the covalent PSM of MOFs.

The first examples of covalent PSM of MOFs were the conversion of a pendant alcohol into an ester, reported in 1999,[3] and the *N*-alkylation of a pyridine ring, reported in 2000.[4] There were no further reports until 2007, and subsequently several groups have reported transformations of amines,[5] including conversions to amides, ureas and salicylidenes. Coupling of azides and alkynes has also been demonstrated[6] and a borohydride reduction has been accomplished.[7] Recently we brought forward our paradigm of tagging MOFs for subsequent PSM and used the classic colorimetric test for the presence of an aldehyde, the formation of its 2,4-dinitrophenylhydrazone, to illustrate this.[8] We define a tag as a group that is stable and non-structure defining during MOF formation, but that can be transformed by PSM. In this communication, we present our efforts to prepare a series of MOFs with sulfur tags. We show that these compounds form a topologically identical series of networks, and demonstrate that the sulfide tags can be converted to sulfones by oxidation while retaining the MOF framework. This is, to the best our knowledge, the first example of an oxidative PSM of a MOF.

We have prepared a series of sulfide-tagged ligands $\mathbf{L^{1-3}}$ (Fig. 1) based on the 4,4′-biphenyldicarboxylate (bpdc) backbone. In all cases the tag group is sufficiently remote from the site of metal complexation for it to play a non-structure defining role during framework assembly.

The solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ with $H_2\mathbf{L^1}$ in DMF (or DEF) at 100 °C over 24 h deposited colourless crystals of a compound that was characterised crystallographically as $[Zn_4O(\mathbf{L^1})_3(DMF)_2]\cdot 4DMF$ **1**.‡ This forms a doubly-interpenetrated cubic network, as shown in Fig. 2. The gross structure is similar to those previously observed for $[Zn_4O(bpdc)_3]$ (IRMOF-9)[9] and the aldehyde-tagged analogue,[8] demonstrating that, as anticipated, the sulfur tag does not play a structure-defining role.

In the structure of **1**, Zn(3), one of the zinc centres of the secondary building unit (SBU), has octahedral geometry due to coordination of two DMF molecules in addition to three carboxylates and the central oxygen atom. This leads to a widening of the angle between two of the carboxylate groups, which can be quantified by a C(16)···O(1)···C(16)′ angle of 107°, which compares with a range of 82°–91° for the other *cis* C···O(1)···C angles. The two interpenetrated networks are closer together in **1** than those in $[Zn_4O(bpdc)_3]$, with a closest Zn···Zn distance of 6.93 Å (*cf.* 8.09 Å in $[Zn_4O(bpdc)_3]$). These structural features help accommodate the tag groups within the pores and were also observed in the hydrazone-functionalised MOF reported previously.[8] Although there is

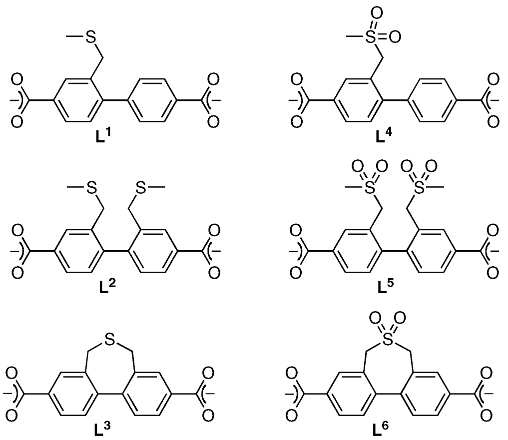

Fig. 1 The functionalised dicarboxylates $\mathbf{L^{1-6}}$. $\mathbf{L^{1-3}}$ were used to generate the sulfur-tagged MOFs **1–3**, whereas $\mathbf{L^4}$ and $\mathbf{L^6}$ were generated by PSM.

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† Electronic supplementary information (ESI) available: Syntheses of $H_2\mathbf{L^{1-6}}$, **1–4** and the post-synthetic modifications of **1** and **3**; X-ray crystallographic data for **1**, **2** and **4**. CCDC 725565–725567. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906170c

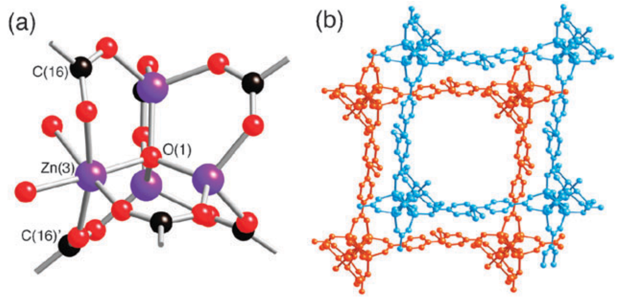


Fig. 2 The structure of **1**. Part (a) shows the SBU and (b) shows the doubly-interpenetrated network, with DMF molecules and hydrogen atoms omitted for clarity.

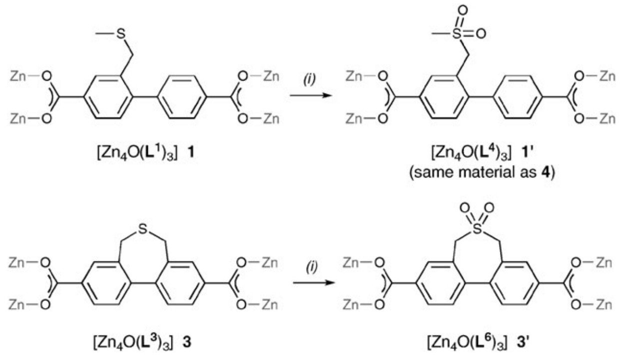
considerable rotational disorder of the phenyl rings in **1**, the sulfide tag groups are remarkably ordered, considering the scope for disorder.

Treatment of $Zn(NO_3)_2{\cdot}6H_2O$ with $H_2\mathbf{L}^{2-3}$ under similar conditions produced crystals of $[Zn_4O(\mathbf{L}^2)_3]{\cdot}5DMF$ **2** and $[Zn_4O(\mathbf{L}^3)_3]{\cdot}n$DMF **3**, respectively.‡ Compounds **2** and **3** also have doubly-interpenetrated cubic structures, but in both cases data quality and disorder of the linkers prevented the tags from being reliably located.

Compounds **1** and **3** were selected for oxidative PSM. In order to help analyse the products of these reactions, the sulfone-functionalised dicarboxylic acids $H_2\mathbf{L}^{4-6}$ were prepared independently. $\mathbf{L}^4$ was converted into a MOF through reaction with $Zn(NO_3)_2$, and the product was structurally characterised as $[Zn_4O(\mathbf{L}^4)_3(DMF)_2]{\cdot}2DMF$ **4**, which again adopts a doubly-interpenetrated cubic network.‡ One of the zinc centres in **4** is coordinated to two DMF molecules, so it displays a distorted octahedral geometry, similar to that observed for Zn(3) in **1**. Significantly, the pendant sulfonyl tags of the $\mathbf{L}^4$ ligands were located in the crystallographic study and refined as being disordered over two positions in a 1 : 1 ratio. As with **1**, the distance between the two networks (closest Zn···Zn contact 7.29 Å) and the opening up of angles proximate to the octahedral zinc centre help to accommodate the functionalities within the pores.

Dimethyldioxirane (DMDO) is a frequently employed reagent for sulfide to sulfone conversion.[10] Given its properties and size we rationalised that it was an appropriate choice of reagent for the oxidative PSM of sulfur-tagged MOFs. The reaction of **1** with DMDO was carried out by soaking 'as-synthesised' crystals of **1** in portions of acetone to exchange for DMF prior to introducing excess DMDO as a dilute solution in acetone (~0.05 M, ~7–8 equiv.) and standing at 4 °C (Scheme 1).‡ We were able to follow the progress of the modification by digesting individual crystals in HCl–H_2O and analysing their composition using electrospray ionisation (ESI) mass spectrometry. During the early stages of the reaction we observed the presence of $[H\mathbf{L}^1]^-$, $[H\mathbf{L}^4]^-$ and considerable amounts of the intermediate oxidation product, the sulfoxide. Near complete conversion of $\mathbf{L}^1$ to $\mathbf{L}^4$ was achieved in 2–3 h, and the reaction was allowed to run to completion overnight as the reagent expired.

The modified crystals **1′** were analysed by powder X-ray diffraction (after standing under DMF) and compared with an authentic sample of **4**. The traces are virtually identical,



Scheme 1 Post-synthetic oxidation of **1** and **3**. (i) DMDO, acetone, 20 °C.

demonstrating that the material derived from PSM is isostructural to that formed by direct reaction, and also confirming that PSM occurs with maintenance of crystallinity and structural integrity of the sample (Fig. 3).

Bulk digestion of the sample in DCl–D_2O followed by analysis by ^{1}H NMR spectroscopy gave a quantitative measure of the reaction. Comparison of the spectrum with those of authentic samples of $D_2\mathbf{L}^1$ and $D_2\mathbf{L}^4$ gave a ratio of $\mathbf{L}^1$: $\mathbf{L}^4$ of 77 : 23, with a small amount of the intermediate sulfoxide also present.

When **3** was treated with DMDO under the same conditions for 3 h, the ESI mass spectra of individual crystals digested in HCl–H_2O showed $[H\mathbf{L}^6]^-$ with no evidence for $[H\mathbf{L}^3]^-$. The quantitative conversion of **3** to $[Zn_4O(\mathbf{L}^6)_3]$ **3′** was confirmed by analysing the ^{1}H NMR spectra of bulk samples digested in DCl–D_2O. These showed only $D_2\mathbf{L}^6$, with no evidence for $D_2\mathbf{L}^3$ or the corresponding sulfoxide. Hence, in this case, the post-synthetic oxidation is 100% efficient.

In conclusion, we have prepared a series of functionalised MOFs that are derived from linear 4,4′-biphenyldicarboxylate ligands bearing substituent sulfur tags. Topologically identical doubly-interpenetrated MOFs are formed from ligands containing chemically different tags (sulfide or sulfone), different numbers of pendant sulfide tags, and tags with different steric and spatial requirements (cyclic or pendant). This demonstrates that the series is robust in its design principle and formation. We were able to post-synthetically oxidise the sulfides to sulfones, and in the conversion of $\mathbf{L}^3$ to $\mathbf{L}^6$, this oxidation goes to completion. To the best of our knowledge these are the first examples of oxidative PSM in MOF chemistry, and this type of reaction increases the scope

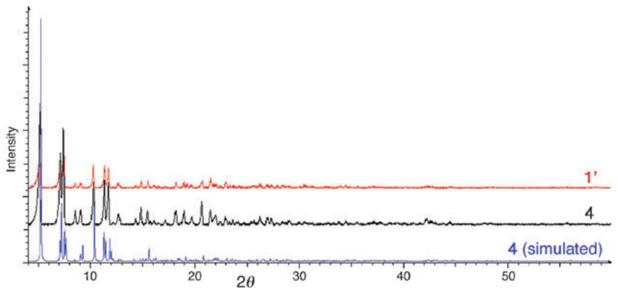


Fig. 3 X-Ray powder diffraction patterns for **1′** and **4** together with the pattern for **4** simulated from the X-ray single crystal data.

of the PSM strategy. Future work on this series of MOF compounds for their inclusion properties and ability to bind metal complexes is currently being pursued.

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Notes and references

‡ *MOF synthesis*: $H_2\mathbf{L^1}$ (0.105 g, 0.35 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.315 g, 1.06 mmol) were dissolved in either DMF or DEF (15 cm^3) and heated in an oven at 100 °C for 24 h. The reaction mixture was allowed to cool slowly to room temperature and crystals of $[Zn_4O(\mathbf{L^1})_3(DMF)_2]{\cdot}4DMF$ **1** were collected by filtration, washed with fresh solvent and air dried. Compounds **2–4** were prepared in an analogous manner.

Post-synthetic oxidation of **1** *to* **1′**: A sample of **1** (0.044 g, 0.027 mmol) was soaked in portions of acetone (3 × 3 cm^3) over 1.5 h to exchange DMF for acetone. The crystals were then covered with a solution of DMDO in acetone (5 cm^3 of 0.05 M solution), and the solution allowed to stand at 4 °C. Individual crystals were taken out, digested in HCl–H_2O and the resulting solutions analysed by ESI-MS. The solvent was removed from the bulk sample by decantation, the crystals washed with acetone and dried under reduced pressure. A sample was digested in DCl–D_2O–d_6-DMSO, and analysis by ^{1}H NMR spectroscopy revealed a sulfide : sulfoxide : sulfone ratio of 19 : 15 : 66.

Post-synthetic oxidation of **3** *to* **3′**: This was undertaken in a similar manner to the conversion of **1** to **1′**. A crystal was taken out after 3 h, digested in HCl–H_2O and the resulting solution analysed by ESI-MS. The solvent was removed from the bulk sample by decantation, the crystals washed with acetone and dried under reduced pressure. A sample was digested in DCl–D_2O–d_6-DMSO, and analysis by ^{1}H NMR spectroscopy revealed complete conversion of sulfide to sulfone.

Crystal data for **1**: $C_{66}H_{78}N_6O_{19}S_3Zn_4$, M = 1617.00, monoclinic, $C2/m$, a = 25.0111(9) Å, b = 22.9843(9) Å, c = 17.1959(3) Å, β = 96.404(4)°, U = 9823.6(5) Å^3, T = 170 K, Z = 4. 83 061 reflections collected of which 10 421 are independent [R_{int} = 0.0698]. R_1 = 0.0765, wR_2 = 0.2190 for 6615 data with $I > 2\sigma(I)$. GOF = 0.997 based on F^2. *Crystal data for* **2**: $C_{69}H_{83}N_5O_{18}S_6Zn_4$, M = 1724.24, hexagonal, $R\bar{3}m$, a = b = 23.8212(3) Å, c = 30.2938(11) Å, U = 14 887.1(6) Å^3, T = 170 K, Z = 6. 84 171 reflections collected of which 3663 are independent [R_{int} = 0.0999]. R_1 = 0.0666, wR_2 = 0.1686 for 1722 data with $I > 2\sigma(I)$. GOF = 0.954 based on F^2. *Crystal data for* **4**: $C_{60}H_{64}N_4O_{23}S_3Zn_4$, M = 1566.81, monoclinic, $C2/m$, a = 25.1670(4) Å, b = 23.2000(3) Å, c = 17.1020(3) Å, β = 93.561(1)°, U = 9966.1(3) Å^3, T = 150 K, Z = 4. 88 639 reflections collected of which 11 661 are independent [R_{int} = 0.0592]. R_1 = 0.0884, wR_2 = 0.2743 for 8102 data with $I > 2\sigma(I)$. GOF = 1.104 based on F^2. **1**, **2** and **4** all contain severely disordered DMF molecules in the pores, and following the use of the SQUEEZE routine these have been taken as 4, 5 and 2 molecules, respectively.

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