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Thermally-Promoted Post-synthetic Pummerer Chemistry in a Sulfoxide-functionalized Metal-Organic Framework

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Reported herein is a thermally-promoted, post-synthetic modification of a zinc metal-organic frameworks pore surface. Sulfoxide tag groups are modified by conventional heating via Pummerer-type chemistry and elimination to aldehyde groups. Simultaneously, a minor competing disproportionation reaction occurs, creating sulfide and sulfone tag groups enhancing the complexity of the pores. The thermal process is gentle, with crystallinity fully maintained, and results in a higher surface area and pore volume for the modified framework.

Introduction

Metal-Organic Frameworks (MOFs) are crystalline materials comprised of organic ligands and metallic nodes which, through self-assembly, form a porous framework. The structures of MOFs can be engineered to possess high surface areas, high porosities and tailored chemical properties on the frameworks surfaces. These tunable properties have made MOFs promising materials for selective gas sorption, asymmetric catalysis, molecular separations, and many other applications.

A means to tune to properties of MOFs is post-synthetic modification (PSM). This strategy involves deliberately modifying the framework after its formation to create desired structural or chemical features in the framework. In terms of the organic component of MOFs, this method offers a pathway to access functional groups and control the degree of ligand functionalization that might not be controlled or achieved by direct synthesis.

A noticeable drawback of many PSMs is the decrease in pore space and surface area that comes about by the modification, either through the addition of groups to the bridging ligands or by damaging the crystal lattice. This can vastly reduce the efficiency of potentially useful MOFs. Consequently, gentle and efficient methods of PSM such as vapour phase techniques are important, as are transformations that maintain or enlarge pore space during PSM.

Three main methods by which pore enlargement is achieved via organic PSM are chemical reagents to effect deprotection, photochemical cleavage and thermal reactions. In each case, groups are cleaved from the bridging ligand, thereby exposing new functionality to the pore surface and increasing pore size.

Thermal modifications, in particular, are quite promising as they require no reagent, are easy to carry out and can be very efficient. For example, Telfer performed a quantitative thermolysis on a zinc MOF with tert-butoxy carbamate tag groups, releasing isobutylene and carbon dioxide, and in doing so exposed amine groups and increased pore space. Stock and co-workers determined that a carboxylic acid-functionalized MOF, Al-MIL-53-COOH, underwent partial decarboxylation (up to 40%) upon heating above 350 °C. While the starting MOF did not admit N₂ gas into its structure, the thermally treated MOF showed porosity. Chanthapally et al. post-synthetically modified alkene-functionalized MOFs by [2+2] photo-induced dimerization and reversed the reaction by heating the MOFs to 120 °C for 12 hours. However, instead of the starting trans-isomer being regenerated exclusively, both cis- and trans-isomers were produced. Morris et al. showed that hemiaminal groups in a functionalised UiO-66 MOF could be driven thermally to aziridines by heating at 85 °C in a vacuum. With increasing time, more aziridine functionality was obtained, and the resulting MOF increased in surface area and capability for adsorption of ammonia.

We have reported reagentless procedures focussed on the concept of post-synthetic rearrangements (PSRs) in MOFs. One benefit of this approach is avoiding chemical reagents in the post-synthetic step as all that is required is ‘front loaded’ in direct synthesis. In this article we report on the thermally-promoted reactions of ligands bearing sulfoxide tag groups in MOFs. With heating, the sulfoxide groups undergo rearrangement and elimination. Additionally, a minor disproportionation side reaction is encountered. The outcomes are an increase in pore space at the same time as changing the MOFs chemical functionality.

For this study, the organic ligand (2-((methylsulfinyl)methyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid, H₂L, was synthesised (Fig. 1). Bridging ligands with similarly substituted sulfoxide groups have been shown to endow MOFs with highly hydrophilic properties, and can be created post-synthetically by oxidizing sulfide groups.
NMR and 13C NMR spectra were obtained using a Varian for 13C. 1H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (d6-DMSO) or 7.27 ppm (CDCl3). For 1H NMR analysis, MOF samples (~5 mg) were digested by adding 35% DCl in D2O (2 µL) and DMSO (500 µL) and waiting until a solution was obtained. Simultaneous thermogravimetric and differential thermal analysis (TG-DTA) data were obtained using a Shimadzu DTG-60 fitted with a FC-60A flow rate controller and TA-60WS thermal analyser. Measuring parameters of 10 °C per min under nitrogen flow (20 %), and DMSO (500 µL) and waiting until a solution was obtained.

**Experimental**

All chemicals used were of analytical grade and purchased from either Sigma Aldrich or Ajax Finechem Pty Ltd. 1H NMR and 13C NMR spectra were obtained using a Varian Mercury VX-300-MHz NMR spectrometer operating at 300 MHz for 1H and 75.5 MHz for 13C or a Varian Inova NMR spectrometer operating at 500 MHz for 1H and 125 MHz for 13C. 1H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (d6-DMSO) or 7.27 ppm (CDCl3). 13C NMR spectra were referenced to the solvent peaks at 38.19, 52.33, 52.39, 57.74, 128.45, 129.42, 130.49, 130.68, 132.49, 143.78, 145.97, 167.01, 167.26.

**Synthetic procedure for dimethyl-((methylthio)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylate**

Dimethyl (2-((methylthio)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylate) (142.4 mg, 0.41 mmol) was dissolved in DCM (4 cm3) and cooled to 0 °C. meta-Chloroperbenzoic acid (164.0 mg, 0.950 mmol) dissolve in DCM (2 cm3) was added drop wise with stirring, with the temperature maintained at 0 °C during addition. The solution was warmed to room temperature over 45 minutes with stirring. The solution was diluted with DCM (20 cm3), washed with water (3 × 20 cm3) and saturated aqueous sodium bicarbonate solution (1 × 20 cm3), dried over sodium sulfate, and evaporated under reduced pressure to leave a solid. This was purified via silica gel column chromatography (Rf, 0.40, 1–1 DCM–EtOAc). Yield = 349.1 mg (95 %). 1H NMR δH (300 MHz; CDCl3) 2.39 (3 H, s) 3.96 (7 H, m) 4.07 (1 H, d, J = 12.60 Hz) 7.42 (3 H, m) 8.08 (1 H, dd, J = 7.50, 1.50 Hz) 8.14 (3 H, m), 13C NMR δC (125 MHz; CDCl3) 38.19, 56.39, 128.91, 129.60, 129.82, 130.29, 130.61, 132.30, 144.05, 146.44, 166.25, 166.58.

**Synthetic procedure for (2-((methylsulfinyl)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylic acid (H2L1)**

1.0 N NaOH (1.0 cm3, 1.0 mmol) added drop wise to a solution of dimethyl-((methylsulfinyl)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylate (142.4 mg, 0.41 mmol) in methanol (3 cm3) and the mixture was stirred overnight. The methanol was removed by rotary evaporation under reduced pressure. The residue was diluted with water (10 cm3) and 1.0 N HC1 was added drop wise with stirring until no more precipitation was observed. The precipitate was filtered and washed with water (3 × 3 cm3). Yield = 127.5 mg (97%). 1H NMR δH (500 MHz; DMSO-d6) 2.46 (3 H, s) 4.03 (1 H, d, J = 13.00 Hz); 4.15 (1 H, d, J = 13.00 Hz); 7.46 (1 H, d, J = 8.00 Hz); 7.55 (2 H, d, J = 8.00 Hz;) 7.97 (1 H, dd, J = 1.00, 7.50 Hz); 8.03 (2 H, d, J = 8.00 Hz); 8.10 (1 H, s); 13.09 (2 H, br s). 13C NMR δC (125 MHz; DMSO-d6) 38.19, 56.39, 128.91, 129.60, 129.82, 129.90, 129.95, 130.29, 130.61, 132.30, 144.05, 146.44, 166.25, 166.58.

**Experimental**

All chemicals used were of analytical grade and purchased from either Sigma Aldrich or Ajax Finechem Pty Ltd. 1H NMR and 13C NMR spectra were obtained using a Varian Mercury VX-300-MHz NMR spectrometer operating at 300 MHz for 1H and 75.5 MHz for 13C or a Varian Inova NMR spectrometer operating at 500 MHz for 1H and 125 MHz for 13C. 1H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (d6-DMSO) or 7.27 ppm (CDCl3). 13C NMR spectra were referenced to the solvent peaks at 39.6 ppm (d6-DMSO) or 77.7 ppm (CDCl3). For 1H NMR analysis, MOF samples (~5 mg) were digested by adding 35% DCl in D2O (2 µL) and DMSO (500 µL) and waiting until a solution was obtained. Simultaneous thermogravimetric and differential thermal analysis (TG-DTA) data were obtained using a Shimadzu DTG-60 fitted with a FC-60A flow rate controller and TA-60WS thermal analyser. Measuring parameters of 10 °C per min under nitrogen flow (20 cm3/min) were used, unless otherwise specified. Powder X-ray diffraction (PXRD) patterns were recorded on a GBC-MMA X-ray diffractometer with samples mounted on 1” SiO2 substrates. Experimental settings in the 20 angle range of 3–30° of 0.04° step size and a scan speed of 3°/min-1 were used for 1 and 0.02° step size and a scan speed of 1°/min-1 were used for 2. Mass spectra were recorded on a Shimadzu LCMS-2010EV electrospray ionisation (ESI) mass spectrometer. Spectra were obtained in negative ion mode using methanol solvent. Freeze drying was carried out in a Christ Alpha 1-2 LDplus Freeze Dryer.

Gas adsorption studies were carried out using a Quantachrome Autosorb MP instrument and high purity nitrogen (99.999 %) gas. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations. Elemental microanalysis was performed by the Chemical Analysis Facility at Macquarie University using a PE2400 CHNS/O elemental analyser (PerkinElmer, Shelton, CT, USA) and PerkinElmer AD-6 Ultra Micro Balance. We found that 1 and 2 (1 in particular) quickly take up atmospheric water during handling in air. No special precautions for protection from atmospheric moisture were taken for the samples sent for microanalysis.
Found C, 60.35%; H, 4.41%; S, 10.05%. \(\text{H}_2\text{L}_1\) (C\(_{16}\)H\(_{14}\)O\(_5\)S\(_1\)) requires C, 60.39%; H, 4.43%; S, 10.05%.

**Synthetic procedure for compound 1**

Zn(NO\(_3\))\(_2\)-6H\(_2\)O (94.2 mg, 0.317 mmol) was added to a solution of \(\text{H}_2\text{L}_1\) (33.6 mg, 0.106 mmol) dissolved in 5.3 cm\(^3\) of \(\text{N}, \text{N}^\prime\text{-dimethylformamide}\) (DMF). The solution was heated in a 100 °C oven for 24 hours and furnished colourless cubic-shaped crystals. The DMF solution was exchanged three times with fresh DMF (2 cm\(^3\)) at 100 °C, and then at room temperature for DCM over 3 days, then for benzene over 2 days. The sample was freeze dried at –53 °C and 0.09 mbar for 1 hour, then heated under vacuum for benzene over 2 days. The sample was freeze dried at –53 °C and 0.09 mbar for 1 hour, then heated under vacuum at 120 °C for 5 hours. Yield = 32 mg (71%).

**Results and discussion**

The ligand \(\text{H}_2\text{L}_1\) was produced in two steps in excellent overall yield starting from dimethyl (2-((methylthio)methyl)-[1,1'-biphenyl]-4,4'-dicarboxylate\(\text{H}_2\text{L}_2\)) by oxidation with \(\text{m}-\text{chloroperbenzoic acid (mCPBA)}\) followed by hydrolysis in basic aqueous solution (Scheme 1).

\[\text{L}^1 \rightarrow \text{L}^2 \text{H}_2\text{L}_1 \rightarrow \text{L}^2\text{H}_2\text{L}_1\]

Scheme 1: Synthesis of \(\text{H}_2\text{L}_1\). (i) m-CPBA, 0 °C, DCM; (ii) NaOH(aq), RT, MeOH.

\(\text{H}_2\text{L}_1\) was reacted with Zn(NO\(_3\))\(_2\)-6H\(_2\)O in DMF at 100 °C for 24 hours to give colourless cubic-shaped crystals \(\text{I}\) (Fig. 1). The structure of \(\text{I}\) was determined by comparison to the MOF formed from (methylsulfonyl)methyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, \(\text{H}_2\text{L}_2\) (see Chart 1), which was shown by single crystal X-ray diffraction to be doubly interpenetrated. Crystals of each MOF were prepared under identical synthesis and activation conditions and compared by powder X-ray diffraction (PXRD) (Fig. S1, ESI). According to the PXRD patterns the peaks are near identical in position and intensity, indicating that \(\text{I}\) is similarly doubly interpenetrated.

A sample of \(\text{I}\) was digested and analysed by \(^1\text{H}\) NMR spectroscopy. This showed the crystals contained 14% of the corresponding sulfone \(\text{H}_2\text{L}_3^1\); resulting in a framework formulation for \(\text{I}\) of 
\[\text{[Zn}_4\text{O(L}^1)^{2.58}\text{(L}^2)_{0.42}\].\]

**Thermally-promoted post-synthetic chemistry**

We have used simultaneous thermogravimetric-differential thermal analysis (TG-DTA) to detect thermally-promoted post-synthetic rearrangements inside porous MOFs. \(^36, 37\)

TG–DTA was used to observe the mass and thermal response of heating \(\text{I}\). The TG-DT measurement of activated \(\text{I}\) recorded under a flowing atmosphere of \(\text{N}_2\) is shown in Fig. 2. The TG trace shows a mass loss of 3.0% up to 90 °C, with a corresponding weak endotherm in the DT trace, indicating a small loss of residual water from the surface of \(\text{I}\). Following this is a strong, sharp exothermic event centred at 230 °C through which a 3.5% mass loss is recorded. Coupled with this observation was the unmistakable and unpleasant odour of methanethiol. Above this temperature, the MOF continues to gradually lose mass until the framework degrades rapidly above 400 °C.

In order to determine the products of the reaction, samples of \(\text{I}\) were heated under nitrogen flow in a TG-DT analyser to 240 °C for held for 30, 180 and 300 minutes to produce samples of MOF 2. These samples were digested and analysed by \(^1\text{H}\) NMR spectroscopy. Four main products were identified from the \(^1\text{H}\) NMR data: the starting sulfoxide ligand, \(\text{H}_2\text{L}_1\), sulfone- (\(\text{H}_2\text{L}_3^1\)) and sulfide-tagged (\(\text{H}_2\text{L}_4^1\)) ligands, and an aldehyde functionalized ligand, \(\text{H}_2\text{L}_5^1\). The structures of these ligands are shown in Chart 1 and the results of the \(^1\text{H}\) NMR data are summarised in Table 1 (see ESI Fig. S8 for \(^1\text{H}\) NMR spectra and Fig. S9 for mass spectrometry data).
According to the presence of these products in the $^1$H NMR spectra, there appears to be two competing reaction pathways. The dominant pathway is Pummerer-type chemistry with elimination of methanethiol to give aldehyde-tagged bridging ligands ($L^4$) (Fig. 3). There are few reports of MOFs tagged with aldehyde groups$^{44}$ and this represents the first post-synthetic method for their installation. The second pathway is disproportionation chemistry, which is indicated by the small increase in sulfone- ($L^3$) and appearance of sulfide-functionalised ($L^5$) bridging ligands in approximately the same proportions. Sulfoxide disproportionation is commonly accepted to come from bimolecular pathways$^{38}$ and this result points to the sulfoxide groups of ligands from different networks interacting to undergo this chemistry. In a previous study,$^{36}$ we saw mass spectrometry evidence for the interpenetrated networks covalently cross linking during a high temperature PSR.

**Table 1.** Ligand compositions in 2 after heating to 246 °C and holding for 30, 180 and 300 minutes.$^a$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$H_2L^1$ (%)</th>
<th>$H_2L^2$ (%)</th>
<th>$H_2L^3$ (%)</th>
<th>$H_2L^4$ (%)</th>
</tr>
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<tr>
<td>0</td>
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<td>14</td>
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<td>-</td>
</tr>
<tr>
<td>30</td>
<td>62</td>
<td>20</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>180</td>
<td>33</td>
<td>27</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>300</td>
<td>25</td>
<td>20</td>
<td>7</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$Performed under $N_2$ flow of 20 cm$^3$ min$^{-1}$.

Gas adsorption studies

We decided to study 1 and 2 by gas sorption for any effects of the modifications on the surface areas and pore volumes. $N_2$ gas sorption data at 77 K was recorded on activated 1 and the same sample was heated under vacuum to 235 °C and held for 180 minutes (to give 2) and the sorption measurements were repeated. Figure 5 shows the isotherms for 1 and 2 and the derived properties of the frameworks are summarised in Table 2. Both 1 and 2 have Type I curves that are typical of microporous materials; however, there is a significant increase in $N_2$ sorption for 2 and the apparent Brunauer-Emmett-Teller (BET) surface area of 2 (2289 m$^2$g$^{-1}$) is substantially higher than 1 (1761 m$^2$g$^{-1}$). Along with this increase in surface area is an increase in pore volume, which rises from 0.72 cm$^3$g$^{-1}$ for 1 to 0.91 cm$^3$g$^{-1}$ for 2. The increase in surface area and pore volume is not surprising given the elimination of methanethiol from the framework results in a smaller size aldehyde group compared to the starting sulfoxide. The change in surface area is quite large (~500 m$^2$g$^{-1}$) and indicates the sensitivity to the number and volume of groups in the pores of 1 and 2. Increases in surface area and pore volume were also seen when groups were chemically,$^{27}$ thermally$^{35}$ or photochemically cleaved$^{36}$ from MOFs. In addition to this, we have seen significant changes in pore volume and surface area brought about through post-synthetic rearrangements where no groups are lost from the framework but the atomic positioning is different.$^{37}$

PXRD data were recorded on activated samples of 1 and 2 (Fig. 4) in order to assess any impacts of the modification process on the crystallinity. The PXRD patterns show 1 and 2 are highly crystalline and share very similar patterns, indicating no change in structure occurs during the thermally-promoted reactions. The excellent maintenance of crystallinity shows that the heating process is gentle on the crystals.
Conclusions

In summary, we have reported a novel thermally-promoted Pummerer-type reaction of a sulfoxide-tagged MOF that ultimately generates aldehyde groups. This example contributes to the building library of thermal organic modifications for MOFs and the simple, gentle and reagentless approach highlights the benefits of thermal methods for post-synthetically modifying MOFs in a single-crystal-to-single-crystal fashion.

Acknowledgements

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Notes and references

42. M. Bryant, A. D. Burrows, P. D. Southon, C. J. Kepert and C. Richardson, unpublished results.