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Post-synthetic pore-space expansion in a di-tagged metal-organic framework

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Post-synthetic pore-space expansion in a di-tagged metal-organic framework

Abstract

A rarely observed example of post-synthetically increasing pore space, while retaining the chemical functionality of the original metal-organic framework is reported. Conventional solvothermal heating in air was used to effect an efficient post-synthetic rearrangement of a bisallyloxy-tagged zinc metal-organic framework. This leads to the pore-space expanded MOF displaying a higher surface area yet lower affinity for CO₂ sorption compared to the original MOF.

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Post-synthetic pore-space expansion in a di-tagged Metal-Organic Framework

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A rarely observed example of post-synthetically increasing pore space, while retaining the chemical functionality of the original metal-organic framework is reported. Conventional solvothermal heating in air was used to effect an efficient post-synthetic rearrangement of a bisallyloxy-tagged zinc metal-organic framework. This leads to the pore-space expanded MOF displaying a higher surface area yet lower affinity for CO₂ sorption compared to the original MOF.

Introduction

Driven by the prospect of applications in gas sorption,^{1a-c} catalysis,^{1d} separations technology^{1e} and as advanced materials in sensors,^{1f} the chemistry of Metal-Organic Frameworks (MOFs) is progressing at a rapid pace. MOF materials are attractive for these functional applications because of their inherent crystallinity in combination with the property of permanent porosity and their potential for purposeful and controlled pore surface modification/engineering.²

Fine-tuning the performance of MOF materials is possible through their modular synthesis from component bridging ligands and metal ions. Another strategy for developing improved MOF materials is through post-synthetic modification, in which it is possible to retain favourable characteristics of the framework. Post-synthetic MOF chemistry is now widely recognised for the benefits it can provide to increase or alter the chemical functionality in MOF materials.³ A problem often encountered utilising post-synthetic chemistry is increasing chemical functionality in the MOF at the expense of diminishing the pore space.^{4a-d} As a result, post-synthetic methods to give chemical functionality and maintain or even enlarge pore-space are important.

Post-synthetically enlarging pore-space in MOFs has rarely been achieved. The two predominant methods for pore-space expansion are photochemical^{5,6} and thermal treatments. The thermal post-synthetic chemistry of MOFs has focussed on the expulsion of small molecules. For example, Telfer demonstrated post-synthetic deprotection chemistry through the breakdown of bulky *tert*-butoxycarbamates to isobutylene and carbon dioxide in a process that unveiled amine groups and enlarged pore space.⁷ Stock and co-workers found that the

aluminium-based MOF Al-MIL-53-COOH was partially decarboxylated (up to 40%) upon heating above 350 °C. In contrast to the unmodified MOF, the desolvated and partially decarboxylated framework admitted N₂ into its structure and, quite remarkably, closes its pores and reverts to its initial non-porous structure by taking up both water and carbon dioxide.⁸ Zeng and Kurmoo found that water was thermally eliminated at 250 °C from pendant hydroxyethyl groups in a zinc-based MOF to give vinyl tag groups to the framework. Unfortunately, this was accompanied by a considerable loss in surface area for the resulting framework.⁹ Also, in related work, Farrusseng used heating to liberate dinitrogen from azides at 150 °C to access nitrenes in MOFs, which were trapped with carbon monoxide and the resulting isocyanates modified further to ureas.¹⁰

We are investigating thermally promoted organic reactions as simple and efficient ways of post-synthetically modifying MOFs. Of interest to us are processes where atoms are not expelled, but can be rearranged after the formation of the MOF—a post-synthetic rearrangement (PSR). Recently, we reported a reagentless, high temperature PSR utilising the aromatic Claisen rearrangement.¹¹ In this article we report a rarely observed case of post-synthetically increasing pore space in a MOF, simply by the rearrangement of atoms on the bridging organic ligand. This subtle change has profound effects on the pore structure of the modified material and brings about a significant increase in surface area.

For this study we chose to work with the bridging ligand 2,5-bis(allyloxy)terephthalic acid, H₂L¹ (Fig. 1). Our interest in this ligand lies in the capacity for the multiple allyloxy tag groups to give MOFs with densely functionalised pore-space. Through multiple PSRs of the allyloxy tag groups, H₂L¹ has the potential to change the pore space and nature of the pore

surface of modified MOFs. This ligand has been used to give analogues of the archetypal MOF-5¹² and $\text{Zn}_2(\text{bdc})(\text{dabco})$ ¹³ frameworks and has been utilised as a ligand for cobalt, zinc and cadmium coordination networks.¹⁴

Experimental

Materials and methods

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. ¹H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (*d*₆-DMSO). ¹³C NMR spectra were referenced to the solvent peaks at 39.6 ppm (*d*₆-DMSO). For ¹H NMR analysis, MOF samples (~10 mg) were digested by adding 35% DCl in D₂O (3 μL) and DMSO (500 μL) and sonicating 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 cm³min⁻¹) were used. Powder X-ray diffraction (PXRD) patterns were recorded on a GBC-MMA X-ray diffractometer with samples mounted on 1" SiO₂ substrates and recorded in the 2θ angle range of 3-30 with a step size of 0.02° at 1° per minute.

IR spectra were obtained using a Shimadzu IRAffinity-1 FTIR, fitted with a MIRacle 10 single reflection ATR accessory. Data collection was performed on Shimadzu IRsolution version 1.50. Mass spectra were recorded on a Waters Quattro Micro ESI mass spectrometer (Milford, Massachusetts, USA). Spectra were obtained in negative ion mode using alcohol/water mixtures.

Gas adsorption studies were carried out using a Quantachrome Autosorb MP instrument and high purity nitrogen (99.999 %) and carbon dioxide (99.995 %) gasses. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations. Elemental microanalysis was performed by the Microanalytical Unit at the Australian National University using a Carlo Erba 1106 automatic analyser. We found that **1** and **2** (**2** 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.

Single crystal X-ray crystallography

Single crystal X-ray diffraction was performed on an Agilent Supernova diffractometer in a stream of cold nitrogen (~120 K) using Cu Kα radiation (λ = 1.54184 Å) for **1** and Mo Kα radiation (λ = 0.71073 Å) for **2**. The crystal structures were solved by direct methods using SHELXS-97 and refined against *F*² on all data by full-matrix least-squares with SHELXL-97 (SHELX-97 program package, Sheldrick, Universität Göttingen, 1997).¹⁵ The data were treated with the SQUEEZE

routine in Platon¹⁶ in an attempt to account for the disordered substituents and solvent molecules. Details on the structural refinements can be found in the ESI to this article.

Synthetic procedure for compound 1

H₂**L**¹ (100 mg, 0.36 mmol) and Zn(NO₃)₂·6H₂O (320 mg, 1.08 mmol) were dissolved in DMF (16 cm³) and heated at 100 °C in an oven for 24 hours. The reaction solution was pipetted away and the crystals were allowed to stand under fresh DMF until required. Following solvent exchange for dry acetone at 80 °C the crystals were dried under high vacuum at 50 °C. Yield 46 mg (35%). **1** Dried: Found: C, 44.59; H, 3.14; N, 0.00. C₄₂H₃₈O₂₀Zn₄ | [Zn₄O(C₁₄H₁₂O₆)₃·H₂O] | [Zn₄O(**L**¹)₃·H₂O] requires C, 44.87; H, 3.41; N, 0.00.

Synthetic procedure for compound 2

As synthesised crystals of **1** were heated in DMF at reflux for 5 h or in DEF at reflux for 0.5 h. For analysis by ¹H NMR spectroscopy, crystals were filtered off and washed with fresh solvent and air dried before digestion in *d*₆-DMSO/DCl. Otherwise the reaction solution was pipetted away and replaced with fresh dry DMF and the solvent heated to reflux for 5 minutes. Full exchange of the remaining solvents was achieved by immersing the samples in portions of dry DCM and heating to 50 °C. The yields were quantitative. **2** Dried: Found: C, 43.82; H, 3.17; N, 0.00. C₄₂H₄₁O_{21.5}Zn₄ | [Zn₄O(C₁₄H₁₂O₆)₃·2½H₂O] | [Zn₄O(**L**²)₃·2½H₂O] requires C, 43.82; H, 3.59; N, 0.00.

Results and discussion

Near colourless cubic crystals, **1**, suitable for analysis by single crystal X-ray diffraction (SCXRD) formed when H₂**L**¹ was reacted with Zn(NO₃)₂·6H₂O in DMF at 100 °C for 24 hours (Fig. 1). **1** crystallises in the cubic space group *Pm-3m* with a unit cell parameter (*a* = 12.80 Å) close to the value found for cubic homoleptic zinc MOFs of structurally related ligands.¹⁷ The analysis confirmed a cubic network with a *pcu* topology and gave a formula of [Zn₄O(**L**¹)₃]·5DMF (see ESI). The SBUs of this structure are crystallographically disordered over two orientations about the same central oxo atom. This leads to two orientations of the coordinating carboxylate groups and to two possible positions of the phenyl ring of the ligand. Due to the disorder inherent in the structure, the pendant allyoxy tag groups could not be found in the crystallographic analysis. However, digestion and solution ¹H NMR analysis of **1** confirmed that **L**¹ was unchanged upon incorporation into the MOF.

Fig. 1 The structure of H_2L^1 and the synthetic conditions to form **1** and **2**.

Post-synthetic rearrangement

We have shown previously that PSRs inside porous MOF structures can be detected through differential thermal analysis.¹¹ The simultaneous thermogravimetric–differential thermal analysis (TG–DTA) measurement of ‘as synthesised’ **1** recorded under an atmosphere of nitrogen gas is shown in Fig. 2. The TG curve shows a mass loss of approximately 36% between room temperature and 170 °C, which would account for ~ 7 molecules of DMF per formula unit, in broad agreement with the formula derived from SCXRD. The weight loss is coupled with strong endothermic peaks in the DT curve, corresponding to the loss of solvents from the framework. A sharp exotherm indicating the rearrangement is then observed to occur in a region with very little mass loss, and well before the framework undergoes major decomposition above 350 °C.

Fig. 2 TG–DTA curves for heating as synthesised **1** to 550 °C. The blue curve shows the TG response. The red curve shows the DT response.

With the PSR temperature being curiously low, we reasoned that the modification could be accessed simply by heating whole crystals in a high boiling solvent. The crystals were heated in refluxing DMF and the extent of the modification was assessed at various time periods through digestion of the

crystals and analysis by 1H NMR spectroscopy. A visual indication of the progress of the modification was the colour of the crystals, as they were observed to turn yellow while maintaining their external form (Fig. S7, ESI). After 5 hours a very high conversion of 15:1 was achieved for coordinated ligands bearing allyl groups compared to allyloxy groups, with only a very small amount undergoing cyclisation to a benzohydrofuran (Fig. S8, ESI). The time could be reduced tenfold to only 0.5 hours by heating in refluxing DEF, and this also improved the rearrangement ratio in the framework to 25:1 as determined by 1H NMR spectroscopy (Fig. S9, ESI). Infrared spectroscopy and electrospray mass spectrometry were also used to establish the structure of H_2L^2 (Fig. S10–S13, ESI).

The high conversion ratios indicate this PSR is very efficient and the heating method is easy to carry out. It is notable that this type of PSM process unveils new hydroxyl functionality but also retains the alkene functionality of the parent MOF. This is different to most PSMs which do not retain the functionality of the parent MOF.

Frameworks modified by heating in DMF or DEF maintained excellent crystallinity as judged by the powder X-ray diffraction patterns (Fig. 3). In fact, the gentle nature of the process allowed the acquisition of high quality single crystal X-ray data on modified crystals (see ESI). The structure of the modified crystals solved and refined best in the cubic space group $Fm-3m$ ($a = 25.76$ Å). The crystallographic analysis confirmed the topology of the framework is unchanged by the modification; however, as in the case of **1**, the pendant tag groups could not be located crystallographically.

Fig. 3 PXRD patterns for **1** and **2**.

Gas adsorption studies

MOF **1** is reported to be non-porous;¹² however, we found exchange of the DMF in the pores was possible for dry acetone at 80 °C and that removal of the acetone under vacuum and gentle heating gave a porous solvent-free framework. Similarly, the activation of **2** was effected by solvent exchange for dry dichloromethane at 50 °C and vacuum drying. The complete removal of solvents from the pores of **1** and **2** was confirmed through digestion and 1H NMR spectroscopic analysis. Figure 4 shows the N_2 sorption isotherms for **1** and **2** at 77 K, and Table

1 summarises surface area and pore volume data. Both **1** and **2** show isotherms typical of microporous MOF materials. Most notably, there is a striking increase in the volume of N₂ adsorbed for **2** as compared to **1**, and the apparent Brunauer-Emmett-Teller (BET) surface area of **2** is significantly higher at 1494 m²g⁻¹ than **1** at 1180 m²g⁻¹. The experimentally obtained surface area for **2** is supported by the calculated value of 1620 m²g⁻¹ for the accessible surface area using the method of Snurr and co-workers.¹⁸ The application of this computational method that calculates the accessible surface area of a ‘perfect crystal’¹⁸ to **1** is complicated by the fully reversible crystalline-to-amorphous transformation of **1** upon activation (Fig. S14, ESI). This phenomenon was also seen by Fisher and co-workers for a related MOF that crystallises in the *Pm-3m* space group.¹⁷

Fig 4. Nitrogen gas adsorption/desorption isotherms for **1** (black) and **2** (red). Closed squares adsorption, open squares desorption. Inset: DFT pore width distributions of **1** (black) and **2** (red).

The increase in surface area can be explained by considering the pore size distributions in the MOFs. DFT calculations based on the adsorption data of **1** clearly show two sizes of pores at ca. 6.6 and 8.5 Å (Fig. 4, inset). The different sizes result from the positioning of the tag groups within the pores. The pore size distribution of **2** shows the depletion of the small pores and a greater contribution of larger pores centred about 8.5 Å. The PSR transfers the allyl groups to carbons of the phenyl ring and this reduces the penetration volume of the pendant groups into the pore-space of **2**. Clearly, this modification has expanded the small pores and we posit that heating serves to thermally anneal the structure towards pores of similar sizes. In our previous study of a biphenyl ligand bearing only one allyoxy tag,¹¹ we found that the pore space was preserved upon PSR. H₂L¹ has two allyoxy tag groups and it could be that the density of the groups augments change to the pore space. We attribute the small hysteresis in the isotherm of **2** to the creation of mesopores on the crystal surfaces induced by the post-synthesis treatment. This type of structural processing¹⁸ has significant potential to influence the structures and performance of MOF materials.

The high current interest in the capture^{1a,b,19} and utilisation^{20,21} of CO₂ by MOFs prompted our investigation of **1** and **2** for

their CO₂ sorption properties (Figs. S15-S18, ESI). Of particular interest was the effect on the sorption properties of the two hydroxyl groups, which are generated through the migration of the allyl groups to the phenyl ring. The CO₂ sorption data at 196 K show that equivalent surface areas and pore volumes were obtained for **1** and **2** compared to the N₂ data at 77 K (Table 1). The value for the heat of adsorption (HoA) extended to zero coverage is also shown in Table 1 and was calculated for **1** and **2** from Virial-type fitting of CO₂ data at 288 and 298 K (Fig. S18, ESI). MOF **1** shows a modest HoA value of 28 kJmol⁻¹ and, interestingly, the HoA value for the pore-expanded MOF **2** is significantly lower at 23 kJmol⁻¹, despite the presence of the hydroxyl groups. This indicates the stronger influence of pore size on the CO₂ uptake properties of these MOFs than the chemical functionality present.^{22,23} It is also possible that the allyl groups may also act to shield the adjacent hydroxyl groups from the adsorptive, thereby reducing their effectiveness.

Table 1. Apparent and calculated surface areas, pore volumes, isosteric heats of adsorption and CO₂/N₂ selectivities for **1** and **2**.

Structure	SA (m ² g ⁻¹) ^a N ₂ (CO ₂)	Pore Volume (cm ³ g ⁻¹) ^b	$Q_{ST}^{CO_2}$ (kJmol ⁻¹) ^c
1	1180 (1022)	0.47 (0.46)	28
2	1494 (1466)	0.61 (0.62)	23

^a Apparent surface area from BET analysis for N₂ at 77 K and for CO₂ at 196 K. ^b At P/P₀ 0.90 for N₂ at 77 K and at 520 torr for CO₂ at 196 K. ^c Calculated from Virial fitting of isotherms recorded at 288 and 298 K.

Conclusions

In summary, we have reported an example where facile heating of a MOF has led to an expansion of the pore-space due to the efficient re-positioning of pendant groups on the bridging ligand. The post-synthetic processing of MOF **1** results in MOF **2** being more ordered MOF and having a higher surface area. However, this appears to come at the expense of affinity for CO₂. This example highlights the subtle and sensitive effects of atomic positioning in MOFs and how this greatly affects the pore structure and performance.

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Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis and characterisation data for H₂L¹, additional TG-DTA data, single crystal data for **1** and **2**, images of crystals, ¹H NMR digestion spectra, MS and IR spectra, gas sorption isotherms, information on isosteric heat of

adsorption calculations and surface area calculations. CCDC 994977-994978. See DOI: 10.1039/b000000x/

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