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Abstract

A thermally promoted postsynthetic rearrangement has been performed on a zinc IRMOF-9-type framework bearing dimethylthiocarbamate tag groups. The rearrangement was accomplished via conventional heating at 285 °C. Crucially, despite the high temperature, the MOF maintains its high accessible surface area and pore space following thermal treatment. The structures and physical properties of the frameworks were characterized by a combination of single-crystal X-ray diffraction, powder X-ray diffraction, differential thermal-thermogravimetric analysis, and gas sorption analysis. The rearrangement results in a slightly higher level of CO₂ adsorption for the modified MOF but with equivalent heat of adsorption. This work offers new perspectives on postsynthetic rearrangements in MOFs and demonstrates that rearrangements that occur at relatively high temperatures are still compatible with the need to retain the structural integrity and porosity of the framework.

Keywords

postsynthetic, rearrangement, dimethylthiocarbamate-functionalized, high, metal-organic, temperature, frameworks

Disciplines

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High Temperature Post-Synthetic Rearrangement of Dimethylthiocarbamate-Functionalized Metal-Organic Frameworks.

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A thermally-promoted post-synthetic rearrangement has been performed on a zinc IRMOF-9 type framework bearing dimethylthiocarbamate tag groups. The rearrangement was accomplished *via* conventional heating at 285 °C. Crucially, despite the high temperature, the MOF maintains its high accessible surface area and pore space following thermal treatment. The structures and physical properties of the frameworks were characterized by a combination of single X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), differential thermal-thermogravimetric analysis (DT-TGA), and gas sorption analysis. The rearrangement results in a slightly higher level of CO₂ adsorption for the modified MOF but with equivalent heat of

adsorption. This work offers new perspectives on post-synthetic rearrangements in MOFs, and demonstrates that rearrangements that occur at relatively high temperatures are still compatible with the need to retain the structural integrity and porosity of the framework.

Introduction

Metal-organic frameworks (MOFs) have seen a huge increase in interest in recent years, due to their potential as porous materials for a wide variety of applications, such as gas sorption and storage,¹⁻⁵ catalysis⁶⁻⁷ and in separations.⁸⁻¹⁰ Reasons MOFs are so attractive for such a wide variety of applications include their crystalline nature, their high porosity and their potential for controlled modifications of their structures and pore surfaces.¹¹⁻¹²

Engineering the performance of a MOF for a specific application can be achieved through direct synthesis using metal ions and bridging ligands with the desired functionality. However, direct synthesis encounters limitations when factors such as solubility or incompatibility with the reaction conditions required are encountered.¹³ Chemical functional groups that cannot be introduced directly can often be installed by post-synthetic modification (PSM).¹⁴⁻¹⁵ Thus PSM has emerged as a useful method for fine-tuning and developing improved MOF materials for applications. Modifications that add bulky groups to the framework are achieved at the expense of pore space.¹⁶⁻¹⁷ As a consequence, new post-synthetic methods that alter the chemical functionality of the MOF and maintain or even enlarge the pore space are crucial to MOF chemistry. This type of PSM is quite difficult to achieve. The main methods used to expand the pore space in MOFs involve photochemical¹⁸⁻²⁰ or thermal reactions. Typically, these reactions cleave a group from the bridging ligand, and serve the dual purpose of increasing pore space in

the MOF by reducing the size of the functional group at the same time as unveiling new functionality.

Thermally-promoted organic modifications of MOFs are promising as they don't require any reagent, which negates chemical-induced damage to the framework and bypasses diffusional problems, and many thermal processes are efficient and operationally easy to carry out. Telfer demonstrated quantitative thermolysis of *tert*-butoxycarbamate groups on IRMOF-10 type frameworks to expose primary amine²¹ and organocatalytically active prolinyl groups²² and this methodology has been utilized now by several other groups.²³⁻²⁷ The MOF Al-MIL-53-COOH is partially decarboxylated when heated above 350 °C. It becomes porous to N₂ but reverts to its non-porous state upon absorption of CO₂ and water.²⁸ Sun *et al.* found that heating a hydroxyethyl functionalized porous zinc-based MOF to 250 °C induced the elimination of water to give vinyl tag groups. However, this PSM resulted in a loss of crystallinity and porosity of the framework.²⁹ The thermally-promoted elimination of water from a non-porous lithium-L-malate coordination polymer above 280 °C was demonstrated and quite remarkably the extent of elimination could be followed by single crystal diffraction.³⁰ Liberation of N₂ from azide-functionalized MOFs at 150 °C to generate reactive nitrenes *en route* to isocyanates has also been reported.³¹

We are interested in thermally-promoted organic reactions to modify MOFs. We utilized the little-known thermolysis of alkyl sulfoxides to generate aldehyde groups in MOFs *via* Pummerer-type chemistry.³² Of particular interest to us are post-synthetic rearrangements (PSRs) and we have reported examples of reagentless PSRs based upon the aromatic Claisen rearrangement in solvent³³ and solventless procedures.³⁴ For this study, we prepared the bridging ligand 2-((dimethylcarbamothioyl)oxy)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, H₂L¹. This ligand

was designed for its potential to form known porous MOF structures with biphenyl dicarboxylate backbones and to undergo the Newman-Kwart rearrangement.³⁵ We are unaware of other MOFs functionalized with dimethylthiocarbamoyl groups and, in light of the high current interest in CO₂ capture technology by MOFs,^{36,37} explored the capability of MOFs laden with these groups for CO₂ adsorption.

Experimental

Materials and methods

All chemicals used were of analytical grade and purchased from Sigma Aldrich, VWR Australia or Ajax Finechem Pty Ltd. ¹H NMR and ¹³C NMR spectra were obtained using either a Varian Mercury VX-300-MHz NMR spectrometer operating at 300 MHz for ¹H and 75.5 MHz for ¹³C, or a Varian Inova-500-MHz 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 in *d*₆-DMSO or 7.26 ppm in CDCl₃. ¹³C NMR spectra were referenced to the solvent peaks at 39.6 ppm in *d*₆-DMSO or 77.7 ppm in CDCl₃. For NMR analysis, MOF samples (~5 mg) were digested by adding 35% DCl in D₂O (2 μL) and *d*₆-DMSO (500 μL) and waiting until a solution was obtained.

Simultaneous differential thermal-thermogravimetric analysis (DT-TGA) data was obtained using a Shimadzu DTG-60 fitted with a FC-60A flow rate controller and TA-60WS thermal analyzer. Measuring parameters of 10 °C per min under nitrogen flow (20 cm³ min⁻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 for 'as synthesized' WUF-1, and a step size of 0.02° at 2° per minute for the activated MOFs.

Gas adsorption studies were carried out using a Quantachrome Autosorb MP instrument and high purity nitrogen (99.999 %) and carbon dioxide (99.995 %) gasses at the Wollongong Isotope and Geochemistry Laboratory. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations. Pore size distributions were calculated using the QSDFT kernel for N₂ at 77 K on carbon with slit/cylindrical pores as implemented in the Quantachrome software (v 3.0). The enthalpy of adsorption as a function of CO₂ loading was calculated by application of the Clausius-Clapeyron equation to CO₂ isotherms measured at 273 K, 288 K and 298 K; the isotherms were interpolated by fitting a cubic spline to the data.

Mass spectra were recorded on a Shimadzu LCMS electrospray-ionization mass spectrometer. Spectra were obtained in negative ion mode in methanol solutions.

Elemental microanalysis was performed on H₂L¹ by the Microanalytical Unit at the Australian National University using a Carlo Erba 1106 automatic analyzer. Elemental microanalysis was performed on the MOFs by the Chemical Analysis Facility at Macquarie University using a PE2400 CHNS/O Elemental Analyzer (PerkinElmer, Shelton, CT, USA) with a PerkinElmer AD-6 Ultra Micro Balance. We found that both MOFs 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. Each was heated at 110 °C for 2 hours and analyzed directly afterwards.

Single crystal X-ray diffraction (SCXRD) data were recorded at room temperature on the MX1 beamline at the Australian Synchrotron operating at 17.5 keV ($\lambda = 0.7085$ Å). Crystals were mounted on a polymer loop after briefly soaking in dibutylformamide. Data indexing and reduction was conducted using the program XDS.³⁸ The structure was solved by direct methods using SHELXT³⁹ and refined using full-matrix least squares against F² using Olex-2.⁴⁰ The

thiocarbamate functional groups of the ligands could not be found in the Fourier difference map. They were introduced to the model in chemically sensible, yet arbitrary, positions and held in fixed positions and with fixed isotropic displacement parameters during refinement. Data are deposited with the Cambridge Structural Database (CCDC 1501497). Data can be obtained for free from www.ccdc.cam.ac.uk

Synthesis of dimethyl 2-((dimethylcarbamothioyl)oxy)-[1,1'-biphenyl]-4,4'-dicarboxylate.

Dimethylthiocarbamoyl chloride (65.0 mg, 0.51 mmol) and DABCO (68.0 mg, 0.61 mmol) were added to dimethyl 2-hydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (140 mg, 0.49 mmol) dissolved in DMA (2 mL) and stirred overnight. The reaction was monitored via TLC and upon completion, the reaction was diluted with H₂O (20 mL) and the product extracted with EtOAc (3 × 15 mL). The extracts were combined and washed with H₂O (5 × 15 mL), brine (15 mL) and dried over anhydrous Na₂SO₄. The solvent was then removed via rotary evaporation. The white solid was triturated with MeOH/DCM, filtered under vacuum and washed with MeOH (2 mL) to give a pure product. Yield 130 mg, (72 %). Found: C, 61.30; H, 5.15; N, 3.74. C₁₉H₁₉NO₅S requires C, 61.11; H, 5.13; N, 3.75. ¹H NMR δ_H (300 MHz; CDCl₃) 3.16 (3 H, s), 3.33 (3 H, s), 3.94 (6 H, s), 7.47 (1 H, d *J* = 8.0 Hz), 7.55 (2 H, d *J* = 8.04 Hz), 7.85 (1 H, s), 7.01 (1 H, d *J* = 7.80 Hz), 8.07 (2 H, d *J* = 8.04 Hz); ¹³C NMR δ_C (75.5 MHz; CDCl₃) 38.58, 43.28, 52.20, 52.33, 125.84, 127.30, 129.05, 129.42, 129.53, 130.55, 130.68, 138.72, 141.35, 150.68, 165.93, 166.80, 186.69.

Synthesis of 2-((dimethylcarbamothioyl)oxy)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, H₂L¹.

1 M NaOH (710 μL, 0.71 mmol) was added drop wise to dimethyl 2-((dimethylcarbamothioyl)oxy)-[1,1'-biphenyl]-4,4'-dicarboxylate (120 mg, 0.32 mmol) dissolved in a 1:1 mixture of MeOH/THF (3 mL) and the reaction stirred overnight. The organic solvents

were removed by rotary evaporation and the residue was diluted with H₂O (15 mL), and then acidified with 1 M HCl to form a white precipitate. The precipitate was collected by vacuum filtration, washed with H₂O (3 × 5 mL) and oven dried at 80 °C overnight. Yield 0.105 g (95%). Found: C, 59.59; H, 4.32; N, 4.03. C₁₉H₁₉NO₅S requires C, 59.12; H, 4.38; N, 4.06. ¹H NMR δ_H (500 MHz; DMSO-*d*₆) 3.20 (3 H, s), 3.25 (3 H, s), 7.60 (3 H, m), 7.68 (1 H, s), 7.90 (1 H, d *J* = 7.81 Hz), 8.01 (2 H, d *J* = 7.81 Hz); ¹³C NMR δ_C (125 MHz; DMSO-*d*₆) 38.60, 43.00, 125.64, 127.09, 129.30, 129.47, 130.38, 130.86, 131.45, 137.87, 140.62, 150.57, 166.50, 167.18, 185.58.

Synthesis of WUF-1. H₂L¹ (110 mg, 0.32 mmol) and Zn(NO₃)₂·6H₂O (250 mg, 0.96 mmol) were dissolved in DMF (15 mL) and heated at 100 °C in an oven for 24 hours. The DMF solution was pipetted away from the resultant pale yellow crystals and replaced with fresh DMF (1 mL) and placed in the oven at 100 °C for 1 hour. This was repeated two more times. The DMF solution was then exchanged with dry CH₂Cl₂ over a week. The MOF was then activated by heating under vacuum at 120 °C for 5 hours. Yield 45 mg (32 %). Found: C, 45.68; H, 3.04; N, 3.01. C₅₁H₄₃N₃O₁₈S₃Zn₄ requires C, 45.60; H, 3.23; N, 3.13.

Synthesis of WUF-2. Activated crystals of WUF-1 were heated under vacuum at 5 °C per minute until 285 °C and held at that temperature for 3 hours. The crystals were then analyzed by DT-TGA, PXRD, gas sorption, and digested in *d*₆-DMSO/DCl for analysis by NMR spectroscopy. The yield was quantitative. Found: C, 44.89; H, 3.16; N, 2.89. C₅₁H₄₃N₃O₁₈S₃Zn₄ requires C, 45.60; H, 3.23; N, 3.13.

Results and discussion

Ligand synthesis and characterization

The ligand H₂L¹ was synthesized in two steps starting from dimethyl-2-hydroxy-[1, 1'-biphenyl]-4, 4'-dicarboxylate,³⁴ as shown in Scheme 1. The dimethylthiocarbamate group was

installed under standard conditions³⁵ in the first step before hydrolyzing the ester groups using aqueous hydroxide. H_2L^1 was obtained as a white solid following acidification with aqueous HCl and characterized by ^1H and ^{13}C NMR spectroscopy (Figures S1 and S2), electrospray mass spectrometry and microanalysis.

Scheme 1. Preparation of the dimethylthiocarbamate-tagged dicarboxylate linker H_2L^1 ^a

^a Conditions: (i) Dimethylthiocarbamoyl chloride, DABCO, DMA (ii) 1 M NaOH, MeOH/THF

MOF synthesis and structural description

WUF-1 (WUF, Wollongong University Framework) was prepared by reacting H_2L^1 with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMF solvent for 24 hours at 100 °C to give pale yellow colored cube-shaped crystals (Figure 1a) suitable for X-ray crystallography using synchrotron radiation. The structure consists of familiar hexacarboxylate Zn_4O SBUs (Figure 1b) reticulated by the linear biphenyl ligands into a cubic-type *pcu* lattice. WUF-1 crystallizes in the space group $C2/m$ as two interpenetrated *pcu* frameworks. The biphenyl backbones of the interpenetrating lattices are separated by *ca.* 3.5-4.5 Å (Figure 1c; Figure S5). We note that other IRMOF-9-type structures with formyl-, allyloxy-, sulfide- and sulfone-tagged biphenyl dicarboxylate ligands crystallize in this space group.^{34, 41-42} The thiocarbamate side groups could not be located on the Fourier map, presumably due to a combination of positional and dynamic disorder. To produce a complete model these groups were introduced in representative positions and held fixed during the refinement.

Figure 1. (a) The structure of H_2L^1 and synthetic conditions for WUF-1 and WUF-2; (b) the structure of the hexacarboxylate Zn_4O SBU; (c) perspective view of the interpenetration of WUF-1.

Post-synthetic rearrangement and characterization

We have shown previously that thermally-promoted PSRs inside porous MOFs are detectable through simultaneous differential thermal-thermogravimetric analysis (DT-TGA).^{33,34} The DT-TGA of 'as synthesized' WUF-1, recorded under an atmosphere of N_2 , is shown in Figure 2. The TG trace shows a mass loss of ca. 35% up to 250 °C in two endothermic steps. This corresponds to the expulsion of occluded solvent. A plateau is seen in the TG curve between 250 °C and 340 °C. During this period there is no mass loss, however a strong exotherm centered at 285 °C is observed in the DT curve. This exothermic process with no mass loss indicates the occurrence of a PSR. Above 340 °C, the MOF gradually begins to decompose and exothermic decomposition is rapid above 400 °C.

Figure 2. DT-TG curve for heating 'as synthesized' WUF-1 to 550 °C (blue curve shows the TG response, the red curve shows the DT response).

WUF-1 was solvent exchanged with CH_2Cl_2 and activated by evacuation of the volatile materials at 120 °C under reduced pressure. A similar procedure was followed with an additional step of heating to 285 °C to produce WUF-2. Activated WUF-1 was analyzed by DT-TGA (Figure S7) and showed the expected exotherm around 285 °C. On the other hand, the DT-TGA for WUF-2 showed no exotherm (Figure S8), implying that the rearrangement had already occurred in the earlier heating step. Samples of each MOF were digested in d_6 -DMSO/DCI for analysis by ^1H NMR spectroscopy and the spectra are shown in Figure 3 (Figure S9). The ^1H NMR spectrum of digested WUF-1 is identical to that of H_2L^1 itself, indicating that no change occurred to the ligand structure during the MOF formation, activation or digestion steps. The ^1H NMR spectrum of digested WUF-2 shows that more than 93 % of L^1 has been converted to L^2 in the PSR. The pattern of H_2L^2 in the aromatic region is distinct from H_2L^1 , and there is a notable change to the protons of the *O*-thiocarbamate (R-OC(=S)NMe_2) from a pattern of two singlets to a broad signal consisting of both methyl groups for the *S*-thiocarbamate (R-SC(=O)NMe_2) (Figure 3). Additionally, negative mode electrospray-ionization mass spectrometry showed identical masses for the L^1 and L^2 anions (Figures S10 and S11), confirming the intact nature of the bridging ligands. Of particular note is the very clean and very high conversion of this PSR and the simplicity and accessibility of conventional heating to achieve the modification.

Figure 3. ^1H NMR spectra of digested WUF-1 (red) and WUF-2 (blue).

The MOFs were examined for their crystallinity after activation using powder X-ray diffraction (PXRD) and the patterns are displayed in Figure 4. The results show that both MOFs have near identical patterns demonstrating that the structure has been unaffected by heating to 285 °C to promote the rearrangement.

Figure 4. PXRD patterns for simulated (black), 'as synthesized' (blue), and activated (orange) WUF-1 and post-synthetically rearranged (pink) WUF-2.

Gas sorption studies

To gain perspective on the porosity and accessible surface areas of the materials, both MOFs were analyzed by gas adsorption isotherms. The N₂ sorption isotherms at 77 K and pore size distributions derived from DFT models are shown in Figure 5 for both MOFs, and Table 1 summarises the surface area and pore volume data. Both isotherms show Type I behavior typical for microporous MOFs and the surface areas are essentially the same. The pore size distributions cluster in a narrow region around a diameter of 9 Å, which is consistent with values from the SCXRD analysis of WUF-1 (Figure S6). Together the PXRD and N₂ sorption data show that crystallinity and porosity is maintained with no structural damage induced by the heating and

rearrangement processes. This is a remarkable result given the high temperature required for the PSR process.

Table 1. Experimental surface areas and pore volumes for WUF-1 and WUF-2

MOF	Apparent Surface Area ($\text{m}^2 \text{g}^{-1}$) ^a	N ₂ Pore Volume ($\text{cm}^3 \text{g}^{-1}$) ^b	CO ₂ Pore Volume ($\text{cm}^3 \text{g}^{-1}$) ^c
WUF-1	1724	7.0	7.3
WUF-2	1760	7.1	7.5

^a From BET analysis for N₂ at 77 K; ^b At P/P_0 0.99 for N₂ at 77 K; ^c At 518 Torr for CO₂ at 196 K

Figure 5. (a) N₂ sorption isotherms at 77 K for WUF-1 (red) and WUF-2 (blue). Filled symbols are adsorption, open symbols are desorption; (b) pore size distributions for WUF-1 (red) and WUF-2 (blue) generated using QSDFT.

With consideration of the polar natures of the *O*- and *S*-thiocarbamate groups, we decided to collect CO₂ sorption data and examine the properties of these MOFs for CO₂ binding. Polar groups, such as amines, are well studied in this regard⁴³ and have been found to show strong binding properties as a result of the interactions that occur between CO₂ molecules and the functionalised pore surface,⁴⁴ where the lone pair of electrons on the amine nitrogen provides a high energy site for CO₂ binding.⁴⁵ Figure 6 illustrates that *O*- and *S*-dimethylthiocarbamate groups have dipolar resonance forms where the oxygen and sulfur atoms carry high electron density and there are different ways CO₂ can interact with these functional groups, including via electrostatics.

Figure 6. Illustration of the resonance forms in *O*- and *S*-dimethylthiocarbamate groups.

CO₂ isotherms were collected at 196 K (Figure S13). The isotherms show rapid uptake of CO₂ and reach saturation around 100 Torr which allows calculation of the pore volumes of the MOFs (Table 1). The results showed slightly higher values compared to those from the N₂ sorption data at 77 K. However, the results for both MOFs are very similar and follow the same trend of WUF-2 having a slightly larger pore volume. Figure 7 shows the CO₂ adsorption data for both MOFs at 273, 288 and 298 K (see Figures S14-S16 for full adsorption-desorption isotherms). The isotherms are essentially linear and the gravimetric uptake of CO₂ at 273 K reaches a maximum of 49 cm³/g for WUF-1 and 56 cm³/g for WUF-2 at 760 Torr. Indeed, at each temperature, higher CO₂ uptakes are observed for WUF-2 and these results are in line with the slightly larger surface area. The calculated heats of adsorption show essentially identical results for both MOFs (Figure

7b), with the values remaining near constant about 15 kJ/mol up to a loading of 1 mmol/g. These values for the heats of adsorption are low compared to values for other polar groups in the literature^{36, 46} and are more consistent with the sorption of CO₂ onto itself.⁴⁷ This might indicate that the CO₂ molecules are unable to interact with high energy sites in the framework, such as the sulfur or oxygen atoms. In the dipolar form, the atoms of the dimethylthiocarbamate groups are coplanar and the adjacent methyl group might have a shielding steric influence on the sulfur or oxygen atoms ability to interact with CO₂. Sterically demanding groups surrounding polar adsorption sites have previously been found to negatively impact on CO₂ adsorption capabilities.⁴⁸ A further reason might be the way the tag groups project into the pores that does not expose the polar sites for adsorption.

Figure 7. (a) The CO₂ adsorption data for WUF-1 (open squares) and WUF-2 (solid diamonds) at 273 K (blue), 288 K (red) and 298 K (black); (b) heats of adsorption for CO₂ adsorption for WUF-1 (red) and WUF-2 (black).

Conclusions

In summary, we have reported a novel example of a high temperature thermal PSR in a MOF bearing dimethylthiocarbamate tag groups. A subtle change in chemical functionality was achieved in a clean and high conversion through simple conventional heating. Although the rearrangement reaction occurs at temperatures much higher than typically employed for thermolysis reactions in MOFs, the conversion was realized with complete retention of structural integrity and without loss of pore space. This work thus offers perspectives for the further expansion of the thermally-promoted post-synthetic chemistry of MOFs. The CO₂ sorption characteristics of the MOFs showed significant levels of uptake, but only moderate heats of adsorption. This might be attributable to the steric bulk and orientation of the tag groups within the pores, which inhibits interactions with CO₂ molecules.

ASSOCIATED CONTENT

Supporting Information.

Supplementary Information (SI) available: ¹H and ¹³C NMR spectra for H₂L¹, DT-TGA data of activated MOFs, an enlarged view of the ¹H NMR digestion spectra, ESI–MS spectra of digested MOFs, an enlarged view of the PXRD patterns, gas sorption isotherms and information on surface area calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

DABCO, 2,4-diazabicyclo[2.2.2]octane; DMA, dimethyl acetamide; DMF, dimethyl formamide, DT-TGA, differential thermal-thermogravimetric analysis; MOF, metal-organic framework, NMR, nuclear magnetic resonance; PSM, post-synthetic modification; PSR, post-synthetic rearrangement; PXRD, powder X-ray diffraction; SCXRD, single crystal X-ray diffraction

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High Temperature Post-Synthetic Rearrangement of Dimethylthiocarbamate-Functionalized Metal-Organic Frameworks.

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Synopsis

We show that very high temperature post-synthetic modifications of metal-organic frameworks can be gentle, with complete retention of the porosity and crystallinity of the parent MOF as evidenced by X-ray diffraction and gas adsorption measurements.