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A post-synthetically reduced borane-functionalised metal-organic framework with oxidation-inhibiting reactivity

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Abstract

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The first post-synthetic reduction of a ketone-containing metal-organic framework (MOF) is reported. The borane tetrahydrofuran complex ($\text{H}_3\text{B}\cdot\text{THF}$) quantitatively reduced a ketone functional group in a porous zinc(II) IRMOF-9 scaffold at room temperature. Single crystal X-ray diffraction studies established that the crystallinity and interpenetration mode of the framework are preserved during reduction. Boron remains bound in the framework and can be removed via mild acid treatment to yield a MOF with identical properties to that prepared by direct synthesis. The boron-functionalised MOF was unable to reduce benzaldehyde but instead was found to inhibit benzaldehyde autooxidation.

Introduction

The pores of metal-organic frameworks (MOFs) can host, orientate, and deliver ‘preinstalled’ substrates for stoichiometric transformations^{1, 2} and stabilise difficult-to-handle species.³ The results show the transformations are predominantly pore-based even though the molecular guests can diffuse from the pores. However, this methodology relies on a high reactant-framework affinity to be successful. Building on this approach, we thought to generate porous, solid-state platforms by tethering reagents to frameworks using post-synthetic modification (PSM). Tethering ensures transformations take place within the pore space, thereby capturing the benefits of size-selectivity. The fundamental difference between MOF reagents and catalysts is the requirement to regenerate the reagent for re-use. Recently, we reported MOF reagents featuring hypervalent iodine oxidants⁴ and elegant work demonstrating this concept comes from Sumby and Doonan.⁵

Amongst the broad scope of MOF PSM, reductions have only seen limited exploration. This is potentially due to the conception that the reaction conditions required to effect these transformations are unsuitable for many MOF structures. For example, one of the first reports of post-synthetic reduction was as part of the two-step sequence to install amino groups on the ligand backbone of Cr-MIL-101, which required SnCl_2 reduction conditions, which are challenging for MOFs.⁶ Burrows and co-workers showed NaBH_3CN reduced imines in aminations of IRMOF-3- NH_2 with differently sized aldehydes. Modest conversions were

achieved (max. 67%) and problems with pore-blocking from boron side-products were noted.⁷

We were firstly interested in developing useful and widely applicable reduction procedures for functional groups in MOFs. Reductions of carbonyl species are desirable as they give access to a variety of functionalities. Yaghi and co-workers reduced aldehyde groups in ZIF-90 in 77% conversion using NaBH_4 in refluxing MeOH for 24 hours and noted higher conversions could be achieved *via* longer reaction times at the cost of decreased crystallinity.⁸ We considered that borane holds advantages as a reagent for carbonyl reduction. Notably, borane has seen very little use in post-synthetic MOF chemistry, with a single report of alkene hydroboration using the dimethylsulfide complex.⁹ Secondly, we considered that since the boron species would remain bound, this could give rise to act as a MOF reagent to reduce other compounds. For example, Wang and co-workers harnessed intrinsic substrate size-selectivity by generating $\text{UiO-66-NH}_2\cdot\text{BH}_3$ and applied it as a reagent in the reduction of differently-sized aldehydes.¹⁰

Herein we show that borane can be loaded post-synthetically in MOFs *via* the reduction of ketone groups or by reaction with alcohol-functionalised frameworks (Fig. 1). We show that the reduction procedure gives a material with identical surface area as material from direct synthesis, demonstrating the effectiveness of the PSM. In addition, a novel mode of reactivity was also found for the borane-loaded frameworks where they acted as autooxidation inhibitors.

Fig. 1 The structures of $\text{H}_2\text{bpdcc(=O)CH}_3$ and $\text{H}_2\text{bpdccCH(OH)CH}_3$ and the interconversions between the frameworks.

Experimental

All chemicals used were of analytical grade and purchased from either Sigma Aldrich, VWR Australia or Ajax Finechem Pty Ltd. The procedures for synthesizing $\text{H}_2\text{bpdcc(=O)CH}_3$ and $\text{H}_2\text{bpdccCH(OH)CH}_3$ are provided in the ESI. ^1H NMR, ^{11}B and ^{13}C NMR spectra were obtained using a Bruker NMR spectrometer operating at 400 MHz for ^1H , 129 MHz for ^{11}B and 101 MHz for ^{13}C . ^1H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (d_6 -DMSO) or 7.27 ppm (CDCl_3). ^{13}C NMR spectra were referenced to the solvent peaks at 39.6 ppm (d_6 -DMSO) or 77.7 ppm (CDCl_3). For ^1H NMR analysis, MOF samples (~5 mg) were digested by adding 35% DCl in D_2O (2 μL) and DMSO (500 μL) and waiting until a solution was obtained.

Simultaneous differential scanning calorimetry and thermal gravimetric analysis (DSC-TGA) data were recorded using a Netzsch STA449F3 at $10\text{ }^\circ\text{C/min}$ under N_2 flow at $20\text{ cm}^3/\text{min}$ for all samples.

Powder X-ray diffraction (PXRD) patterns were recorded on a GBC-MMA X-ray diffractometer with samples mounted on $1''$ SiO_2 substrates. Experimental settings in the 2θ angle range of $3\text{--}30^\circ$ with 0.02° step size and 1° min^{-1} scan speed were used for all samples.

Single crystal X-ray diffraction (SCXRD) data for **WUF-30** were collected on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator ($\text{Cu K}\alpha$ radiation, $1.54180\text{ \AA}$), fitted with high flux Osmic multilayer mirror optics, and a curved image-plate detector. Data were collected at 292 K under $d^*\text{TREK}$ and were integrated and scaled and averaged with FS-Process.¹¹ Single crystal diffraction data for **WUF-31** were collected using a Bruker D8 Venture diffractometer equipped with a $\text{I}\mu\text{S}$ Diamond source ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54180\text{ \AA}$) and a Photon CPAD detector at 292 K. The data were integrated and scaled and averaged with APEX 3.¹² 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-97.¹³

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. Freeze drying was carried out in a Christ Alpha 1-2 LDplus Freeze Dryer. Elemental microanalysis was performed by the Chemical Analysis Facility, Macquarie University, Australia.

Synthetic procedure for WUF-30

$\text{H}_2\text{bpdcc(=O)CH}_3$ (0.377 g, 1.33 mmol) and $\text{Zn(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.19 g, 3.99 mmol) were dissolved in DMF (45 mL) and divided even between eight 20 mL vials. The vials were capped and heated in an oven at $100\text{ }^\circ\text{C}$ for 24 hours. The resultant orange coloured crystals were consolidated and the DMF exchanged 3 times with fresh DMF at $100\text{ }^\circ\text{C}$. The crystals were solvent exchanged into CH_2Cl_2 and then cyclohexane for storage. Found: C, 50.17%; H, 3.08%; $[\text{Zn}_4\text{O}(\text{bpdcc(=O)CH}_3)_3]\cdot 1.5\text{H}_2\text{O}$ requires C, 50.05%; H, 2.89%.

Synthetic procedure for WUF-31

The same procedure as above was used with $\text{H}_2\text{bpdccCH(OH)CH}_3$ (0.481 g, 1.68 mmol) and $\text{Zn(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.50 g, 5.04 mmol) and DMF (50 mL). Found: C, 50.15%; H, 3.59%; $[\text{Zn}_4\text{O}(\text{bpdccCH(OH)CH}_3)_3]\cdot \text{H}_2\text{O}$ requires C, 50.18%; H, 3.34%.

Synthetic procedure for WUF-32

A solution of 1 M $\text{H}_3\text{B}\cdot\text{THF}$ complex (0.89 mL, 0.89 mmol) in dry, nitrogen-sparged cyclohexane (1 mL) was layered over crystals of $\text{Zn}_4\text{O}(\text{bpdcc(=O)CH}_3)_3$ (~100 mg) in a nitrogen-flushed stoppered vial and left to stand for 72 hours. The crystals were then exchanged three times with fresh nitrogen-sparged cyclohexane over two days and stored in dry cyclohexane under a nitrogen atmosphere.

Synthetic procedure for PS-WUF-31

A solution of glacial acetic acid (6 μL , 0.104 mmol) in anhydrous THF (1 mL) was layered over crystals of $\text{Zn}_4\text{O}(\text{bpdccCH(OBHO}^t\text{Bu)CH}_3)_3$ (**WUF-32**) (~50 mg) in the minimum of dry THF. The acetic acid/THF solution was removed and replenished twice more over two days. The crystals were then solvent exchanged with fresh dry cyclohexane three times over a period of three days.

Results and discussion

Ligand synthesis. 2-Acetyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid ($\text{H}_2\text{bpdcC(=O)CH}_3$) was prepared from dimethyl 2-formyl-[1,1'-biphenyl]-4,4'-dicarboxylate¹⁴ by Grignard addition of methylmagnesium bromide, oxidation using Jones reagent and acid hydrolysis, as shown in Scheme 1. 2-(1-Hydroxyethyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid ($\text{H}_2\text{bpdcCH(-OH)CH}_3$) was obtained after hydrolysis of the respective dimethyl ester compound in aqueous base and an acidic workup. We also synthesized $\text{H}_2\text{bpdcCH(-OH)CH}_3$ via a different seven-step sequence and report the full details in the ESI. The diacid compounds were characterised by ^1H and ^{13}C NMR spectroscopy and microanalysis.

Scheme 1: Synthetic pathway to $\text{H}_2\text{bpdcC(=O)CH}_3$ and $\text{H}_2\text{bpdcCH(-OH)CH}_3$; (i) MeMgBr , THF, 0°C ; (ii) Jones Reagent, acetone, rt; (iii) 6M HCl , reflux; (iv) 1M NaOH , MeOH/THF , rt.

MOF synthesis and characterisation

The targeted MOF system for this study was the interpenetrated **pcu** frameworks of IRMOF-9, which is established as a reliable system for the incorporation of functionalised ligands.^{14–21} The pore sizes, typically around $9\text{ \AA}$ for such functionalised frameworks, are large enough for diffusion of $\text{H}_3\text{B}\cdot\text{THF}$ throughout the pore system.

Preparations of the MOFs were carried out by heating the respective ligands with excess $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in DMF solutions at 100°C . Orange cubic-shaped crystals formed in the reaction of $\text{H}_2\text{bpdcC(=O)CH}_3$ (**WUF-30**) while crystals from the reaction of $\text{H}_2\text{bpdcCH(-OH)CH}_3$ (**WUF-31**) were similarly shaped, but pale yellow in colour.

Single crystal X-ray diffraction (SCXRD) analysis showed **WUF-30** and **WUF-31** crystallise as the expected interpenetrating networks in the space group $P4_21m$.

Descriptions and images (Fig. S4–S5) of the asymmetric units can be found in the ESI. Recently, we classified the interpenetration modes in IRMOF-9 and derivatives.¹⁷ **WUF-30** and **WUF-31** crystallise as type II, where SBUs of each net are situated centrally and proximate to a face of the other framework (Fig. 2a). Square ($\sim 8 \times 8\text{ \AA}$) and rectangular ($\sim 15 \times 7\text{ \AA}$) pores run along the $[001]$ and $[100]$ directions, respectively, with the largest pore system ($\sim 10 \times 10\text{ \AA}$) running parallel to the $[110]$ direction, as shown in Fig. 2 and in the supplementary movie provided (ESI). The closest contacts between the interpenetrated networks occur around the midpoints of the biphenyl linkers (ca. $3.9\text{ \AA}$ between closest phenyl ring carbons). This is where the tag groups reside; however, the acetyl and hydroxyethyl groups were not located on Fourier maps, which we attribute to a combination of positional and rotational disorder. These groups were incorporated in the crystallographic models in chemically sensible positions.

^1H NMR spectra, obtained after vacuum drying and digestion of the MOFs with DCl in d_6 -DMSO, confirmed the ligands are incorporated without change into the crystals (Fig. 3). Following these analyses, the solvent-free frameworks could be formulated as $\text{Zn}_4\text{O}(\text{bpdcC(=O)CH}_3)_3$ for **WUF-30** and $\text{Zn}_4\text{O}(\text{bpdcCH(-OH)CH}_3)_3$ for **WUF-31** and these were supported by microanalyses.

Fig. 2 Views of the pore systems in the interpenetrating networks of **WUF-30** and **WUF-31**. (a) along the 001 direction, (b) along the 100 direction, (c) along the 110 direction. Tag groups and hydrogen atoms are not shown for clarity.

The PXRD patterns of as-synthesised $\text{Zn}_4\text{O}(\text{bpdcC(=O)CH}_3)_3$ and $\text{Zn}_4\text{O}(\text{bpdcCH(-OH)CH}_3)_3$ showed peaks at 2θ values of 5.2° , 7.3° , 10.3° , 11.5° , 15.5° and 20.7° that match the positions in calculated patterns (Fig. S7), confirming the phase-purity of the bulk MOF samples.

ARTICLE

Fig. 3 ^1H NMR spectra of digests in $\text{DCl}/d_6\text{-DMSO}$ of $\text{Zn}_4\text{O}(\text{bpdcC}(=\text{O})\text{CH}_3)_3$ (**WUF-30**) (blue), $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ (**WUF-31**) (purple), $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OBHO}^t\text{Bu})\text{CH}_3)_3$ (**WUF-32**) (black) and $\text{PS-Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ (**PS-WUF-31**) (orange). The resonance asterisked in the spectrum of **WUF-30** is the ketone group. The signals asterisked with triangles in the spectra of **WUF-31**, **WUF-32** and **PS-WUF-31** are the methyl protons of hydroxyethyl groups. The resonances coloured red in the spectrum of **WUF-32** are for 1-butanol.

Post-synthetic reduction chemistry

$\text{Zn}_4\text{O}(\text{bpdcC}(=\text{O})\text{CH}_3)_3$ was quantitatively reduced by exposure to approximately 10 equivalents of $\text{H}_3\text{B}\cdot\text{THF}$ over three days at room temperature. The crystals maintained their lustre and morphology while turning a pale-yellow colour during their reactions with $\text{H}_3\text{B}\cdot\text{THF}$. Decent quality SCXRD data could be obtained on the modified MOF (ESI). This analysis determined that the mode of interpenetration remained the same; however, in the space group $P4_21c$ (Fig. S6).

Figure 3 shows the ^1H NMR digestion spectrum of the product from the reduction reaction. The match for all the C-H signals of $\text{bpdcCH}(\text{-OH})\text{CH}_3$ and the reduction product, in conjunction with the complete absence of the ketonic methyl group signal at 2.21 ppm, confirmed the quantitative conversion. Also evident in digestion spectra of the modified materials after activation was 1-butanol. We attribute the origin of this to ring-opening of THF coordinated to the boron in the framework. ^1H NMR integration of these signals revealed an equimolar ratio with the ligands, strongly suggestive of the structure shown in Fig. 4. Ring-opening of THF is common in unstabilised BH_3 solutions and is accelerated at higher temperatures.²²⁻²⁴ In our procedure, the

NaBH_4 stabiliser is removed by exchange with fresh solvent and our protocol also involved heating at 80 °C under vacuum before analyses facilitating the ring opening observed.

Fig. 4 Postulated mechanism for generating butanolate in **WUF-32**.

The amount of bound borane in **WUF-32** was quantified by inductively coupled plasma-mass spectrometry (ICP-MS) after activating and digesting the modified MOF. The boron to zinc ratio of 0.91 (Table S2) is higher than that expected from the molecular formula (0.75). Li and co-workers found that ammonia borane coordinated to metal nodes within a yttrium MOF.²⁵ Consequently, the binding of boron species to any unsaturated metal nodes or defect sites may account

for additional boron. Importantly, this analysis confirmed that boron remained bound to the MOF upon reduction of the ketone functionality. As the reduction has not been quenched by a source of Brønsted acid, we reasoned the borane remains bound to the alkoxide. A second pathway to load borane was effected by exposing $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ to $\text{H}_3\text{B}\cdot\text{THF}$. ICP-MS analysis revealed a boron to zinc ratio of 0.50 in the digested MOF, representing a 66% conversion. We expect this could be raised by exposure to more equivalents of reagent.

As mentioned in the introduction, removing boron by-products from hydride-based functional group reductions in MOFs appears problematic.⁷ We found the bound boron could be removed efficiently by washing the MOF with dilute acetic acid solutions in dry THF at room temperature, with ICP-MS analysis showing only trace amounts of boron present after this protocol (Table S3). IRMOFs are well-known for their intolerance to aqueous acid, so we employed dilute non-aqueous conditions here. The ^1H NMR spectrum of the acid-washed MOF showed no signals corresponding to 1-butanol but did show a small amount of acetic acid (Fig. 3), even after repeated solvent exchange, suggesting to us the binding of acetate at defect sites. Therefore, the two-step protocol of $\text{H}_3\text{B}\cdot\text{THF}$ treatment and acid washing quantitatively post-synthetically reduces $\text{Zn}_4\text{O}(\text{bpdcC}(=\text{O})\text{CH}_3)_3$ to the material hereafter referred to as PS- $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ (PS = Post-Synthesis).

The experimental PXRD traces for $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OBHO}^t\text{Bu})\text{CH}_3)_3$ and PS- $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ (Fig. S7) showed defined peaks indicating highly crystalline material after borane treatment and after acid washing. Also, the almost identical traces of as-synthesised $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ and PS- $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ confirmed the materials are isostructural.

Reaction studies

With the successful and complete loading of borane, we wondered if $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OBHO}^t\text{Bu})\text{CH}_3)_3$ (**WUF-32**) could function as a very weak hydride donor, possibly capable of effecting reductions. As an exploratory investigation we looked the reaction with benzaldehyde, which based on its kinetic diameter of ~ 6 Å should readily enter the pores for interaction with the borane species.

The reaction was monitored via an *in situ* ^1H NMR experiment in d_6 -benzene of **WUF-32** and benzaldehyde, with anisaldehyde as an external standard. Spectra recorded out to 72 hours showed no reduction of the benzaldehyde signals or appearance of signals for benzyl alcohol. In addition, ^1H NMR spectroscopy of the digested MOF after the experiment confirmed no reaction trapping benzaldehyde or benzyl alcohol had taken place, as only signals corresponding to $\text{bpdcCH}(\text{-OH})\text{CH}_3$ were present.

An intriguing result was seen in the control study using $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ in place of the borane-functionalised MOF. ^1H NMR spectra in this experiment revealed the formation of benzoic acid after six hours. This

increased across the three-day period with a proportionate decrease in benzaldehyde (Fig. S12). Isolation from the supernatant solution and NMR spectroscopic and melting point comparisons to an authentic sample confirmed the assignment. A second control experiment with only benzaldehyde present in solution showed exactly the same performance, signifying $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ played no role in the conversion.

Benzaldehyde undergoes autooxidation when exposed to O_2 via a radical chain process.^{26, 27} Thus, this oxidation was likely due to aerial exposure during the NMR experiment. We see two ways by which the borane-functionalised MOF could inhibit this process. The first is by reacting directly with dioxygen²⁸ and the second is by quenching an intermediate along the autooxidation pathway.²⁶ The latter seems more likely given the reduced reactivity compared to other borane species and the weakly hydridic nature of the B-H bond in the group.

Thermal analysis and gas adsorption

Activation of the MOFs for gas adsorption and differential scanning calorimetry-thermal gravimetric analysis (DSC-TGA) studies was achieved through solvent exchange into cyclohexane, freeze-drying and heating under dynamic vacuum for 5 hours at 80 °C. DSC-TGA on activated $\text{Zn}_4\text{O}(\text{bpdcC}(=\text{O})\text{CH}_3)_3$ (**WUF-30**) under an atmosphere of N_2 showed no mass loss before 450 °C (Fig. 5; Fig. S8), after which point the mass loss is coupled with decomposition. $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$ (**WUF-31**) performed similarly until 450 °C (Fig. 5; Fig. S9) and then undergoes a series of thermal events indicative of decomposition. Sun *et al.* reported the thermal dehydration of hydroxyethyl groups to vinyl groups within a zinc MOF around 250 °C, however, no such reactivity was observed here for $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OH})\text{CH}_3)_3$.²⁹ The performance of $\text{Zn}_4\text{O}(\text{bpdcCH}(\text{-OBHO}^t\text{Bu})\text{CH}_3)_3$ (**WUF-32**) was very different (Fig. 5; Fig. S10). This MOF shows a series of mass losses with a notable endotherm and mass loss at 115 °C, which is close to the boiling point of 1-butanol. The trace then shows continuous mass loss out to 350 °C, which we attribute to gradual thermal decomposition of the boron-containing side group.¹⁰ After 350 °C, there is a period of stability before undergoing decomposition at the same temperature as the other frameworks.

Fig. 5 TGA traces of **WUF-30** (blue), **WUF-31** (purple) and DSC-TGA trace for **WUF-32** (orange).

We measured N₂ gas adsorption isotherms at 77 K for all the MOFs as we have found this to be a sensitive measure of framework integrity following PSM.^{16, 21, 30, 31} The adsorption legs of the isotherms are shown in Fig. 6 with full adsorption-desorption isotherms provided in Fig. S13 and the N₂-accessible BET surface areas and pore volumes presented in Table 1. In general, each MOF shows a type I isotherm with very similar uptakes. Notably, the total gas uptake for PS-**WUF-31** is only very slightly reduced compared to **WUF-31** from direct synthesis. Furthermore, the BET surface areas are essentially the same and DFT analysis (Fig. S13) showed no change in the pore size. This demonstrates that this PSM protocol is gentle and delivers material directly comparable to direct synthesis.

Fig. 6 Nitrogen gas adsorption isotherms at 77 K for **WUF-30** (blue), **WUF-31** (purple) and PS-**WUF31** (orange).

Table 1. N₂-accessible BET surface areas and pore volumes.

	SA (m ² g ⁻¹) ^a	Pore Volume (cm ³ g ⁻¹) ^b
WUF-30	2180	0.867
WUF-31	2084	0.810
PS- WUF-31	2042	0.831

^a From BET analysis for N₂ adsorbate at 77 K ^b At P/P_0 0.95.

Conclusions

Isostructural ketone- and hydroxyethyl-functionalised IRMOF-9 frameworks were synthesised and characterised. Borane-loading was effected using H₃B·THF to reduce the ketone groups in Zn₄O(bpdcC(=O)CH₃)₃ and to react with hydroxyethyl groups in Zn₄O(bpdcCH(-OH)CH₃)₃. Mild acid treatment removed the coordinated borane species giving PS-Zn₄O(bpdcCH(-OH)CH₃)₃, with identical properties to the material from direct synthesis. The mild conditions for conversion and successful removal of boron side-products, which proved troublesome in other post-synthetic reductions, points to the potential for wide applicability of this protocol, even to fragile MOF structures.

Applying Zn₄O(bpdcCH(-OBHO^tBu)CH₃)₃ as a MOF reagent for reduction of benzaldehyde was unsuccessful.

However, we found that this MOF inhibited the autooxidation of benzaldehyde. This result uncovers a new direction for MOFs as useful porous reagents.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

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Electronic Supplementary Information (ESI) available: synthetic procedures for H₂bpdcC(=O)CH₃ and H₂bpdcCH(-OH)CH₃, ¹H and ¹³C NMR spectra for H₂bpdcC(=O)CH₃ and H₂bpdcCH(-OH)CH₃, ¹H and ¹¹B NMR digestion spectra for **WUF-32** and **PS-WUF-31**, crystallographic tables and descriptions of asymmetric units and refinements, DSC-TGA data, PXRD traces, gas adsorption isotherms and surface area calculations. CCDC 2012649-2012650.

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