Framework functionalisation triggers metal complex binding†

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Post-synthetic derivatisation of a porous material produces a functionalized material that binds the metal complex V(O)acac$_2$, in contrast to the unfunctionalized precursor, which is inactive for complex binding.

Metal organic frameworks (MOFs) are a relatively new family of porous materials constructed from multi-dentate organic building blocks linking metal centres. A significant advantage in the synthesis of MOF materials over the ubiquitous zeolites is the large variation possible in the chemical composition of the linker group.[1] This is crucial as the chemical nature of the chosen linker controls the surface pore environment; thus specific properties can be engendered simply by linker modification.[2] Of particular interest are frameworks generated from multi-functional linkers, where one moiety is employed in material construction (binding to the metal nodes) whilst the second remains accessible (metal-free) for further use (*e.g.*, catalysis, sensing, separation).[3–7] The direct, one step, synthesis of MOFs with desirable secondary functional groups, barring a number of notable exceptions,[1,8] has proven problematic, principally due to their chemical/thermal sensitivity combined with an inherent tendency to undergo irreversible metal complexation.[9,10] An alternative methodology for generating accessible pore wall functionalities is a two step approach, involving initial framework synthesis followed by functional group transformation.[11,12] This involves pore surface groups that are not integral to the framework structure being covalently modified using established solution phase chemistry. The gross extended framework structure will remain unchanged, but surface functionalisation will generate a distinct pore topology combined with altered chemical properties. $[(Zn_4O)(O_2C–C_6H_3(NH_2)–CO_2)_3]_n$, IRMOF3 (iso-reticular MOF3), is a porous MOF decorated with pendant amine ($–NH_2$) groups previously developed by Yaghi *et al.*[1] The amine moieties are not intimately involved in the framework backbone, and therefore are available to undergo chemical transformations; indeed during this work the conversion of the amine group quantitatively to an amide functionality has been reported.[11] In this paper we report a more desirable amine transformation *via* a simple condensation reaction producing a salicylidene (R–N=C–C_6H_4OH) moiety, useful as a bidentate ligand. Salicylidene formation activates the framework towards metal sequestering, demonstrated by heterogenizing a vanadyl complex; in contrast, the unfunctionalised parent material, possessing only NH_2 groups, displays no propensity for metal binding.

IRMOF3 was prepared as previously reported,[13] but to alleviate the inherent moisture sensitivity post activation by chloroform,[14–16] a further guest exchange for toluene was performed. This generates a toluene solvated material, IRMOF3-tol$_x$ ($x \approx 5$ by micro and thermogravimetric (TG) analysis).† This toluene impregnation enables manipulation of activated material in ambient conditions (air) for short periods (<30 minutes) with no degradation observed, judged by phase purity (by X-ray powder diffraction (XRPD)) and high porosity (consistently >80 weight% CO_2 uptake at 195 K and 1 bar CO_2 pressure). In addition, samples stored in 'wet' (standard analytical reagent grade with no drying) toluene for months show no decomposition (by XRPD and porosity measurements). An identical procedure can be applied to significantly increase the moisture resistance of the closely related material MOF-5, $[(Zn_4O)(O_2C–C_6H_4–CO_2)_3]$. No analogue of the water-derived material, MOF69c,[17] is observed during similar handling procedures. The enhanced framework stability afforded by toluene guest molecules can be attributed to the combination of enhanced framework–guest interactions and toluene's lower volatility (relative to $CHCl_3$), both of which have the effect of reducing the effective vapour pressure of the guest molecules. A highly pertinent calculation revealed that benzene adsorbed in MOF-5 resides in pockets surrounding the moisture sensitive Zn_4O cluster.[18] This is consistent with the observed enhanced stability of toluene activated IRMOF materials as arene encapsulation of the Zn_4O cluster would form a hydrophobic barrier, preventing H_2O attack. Derivatisation of IRMOF3-tol$_x$ is achieved by the addition of two equivalents (per NH_2 group) of salicylaldehyde to a toluene suspension of IRMOF3-tol$_x$ and allowed to stand for 7 days, followed by toluene washing.

Functionalisation produced a partially converted MOF, IRMOF3-sal$_{0.4}$ (Fig. 1), with empirical formula (Zn_4O)-$(O_2C–C_6H_3(NH_2)–CO_2)_{2.6}$ $(O_2C–C_6H_3–(N=C(H)C_6H_4OH)–CO_2)_{0.4}$, isolated as the toluene solvate.† The degree of amine conversion is determined from a desolvated (80 °C, 18 h, 1×10^{-3} torr) elemental analysis.† Successful imine formation was initially indicated by micro-crystallite colour change from cream to yellow, indicative of imine formation, an observation confirmed by the solid state UV/Vis spectra, with an IRMOF3-sal$_{0.4}$ adsorption centred at 450 nm characteristic of the salicylidene moiety.† Crystallinity is maintained throughout the conversion (by XRPD); furthermore the

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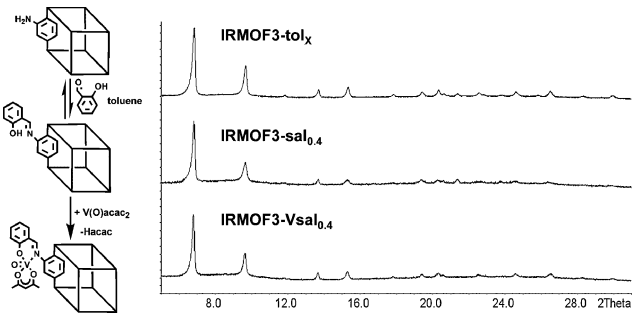

Fig. 1 Left, schematic for the functionalisation of IRMOF3 with salicylaldehyde and subsequent binding of a vanadyl complex (acac = acetylacetonate). Right, XRPD (5 to 30° 2θ) for each material.

similar peak positions and relative intensities observed for IRMOF3 and IRMOF3-sal$_{0.4}$ allow us to conclude that there are minimal changes to the extended lattice. There is no observable evidence (by XRPD) for any decomposition initiated by the stoichiometric formation of the H_2O by-product. The salicylidene functionalisation can be performed on single crystals with no reduction in crystallinity, but subsequent single crystal X-ray diffraction on IRMOF3-sal$_{0.4}$ proved uninformative. The inherent positional disorder of the aryl–NH_2 group in IRMOF3 combined with a lack of long range order that arises due to the partial conversion to imine frustrated attempts to locate the salicylidene.[11]

Unambiguous confirmation of imine formation was forthcoming from the solid-state ^{1}H–^{13}C CP/MAS NMR spectra (Fig. 2) on evacuated materials. The appearance in the IRMOF3-sal$_{0.4}$ spectrum of two resonances (162 and 158 ppm) assignable to *C*=N and aryl *C*–OH; in addition to the more complex *C*O_2 and aryl *C*–H regions in IRMOF3-sal$_{0.4}$ are consistent with additional overlapped resonances due to randomly arranged functionalized (~13%) and unfunctionalized (~87%) amino-terephthalates in IRMOF$_3$-sal$_{0.4}$. Importantly no aldehyde (*C*=O) resonance is observed at *ca.* 195 ppm, precluding impregnation by unreacted salicylaldehyde. The ^{1}H fast MAS NMR spectrum post-functionalisation is also informative revealing a resonance at 13.4 ppm attributable to a hydrogen bonding OH moiety (salicylidene OH hydrogen bonded to imine N), the chemical shift is fully consistent with other reported strong hydrogen bonded resonances in organic solids.[19] IR spectroscopy is less revealing with the framework *CO*$_2$ and *NH*$_2$ stretching bands dominating, thus obscuring any imine (C=N) and O–H stretches. The functionalized framework IRMOF3-sal$_{0.4}$ remains highly porous, but does adsorb 2 mass% less CO_2 (at 195 K and 1 bar CO_2) than the starting material IRMOF3,† confirming the expected decrease in void space post functionalisation, further corroborated by a reduction in the degree of solvation of IRMOF3-sal$_{0.4}$ (by TGA). A control reaction with amine-free material, MOF-5 (2 eq. of salicylaldehyde per aryl group, 7 days), resulted in no salicylaldehyde incorporation,† fully consistent with covalent tethering being a prerequisite for salicylaldehyde incorporation and not simply physisorption by strong host–guest interactions.

The observed sub-stoichiometric conversion (*ca.* 13% of amine groups react) corresponds to only 0.4 salicylidene groups per cavity (there is one cavity per empirical formula unit). This value is significantly below that expected for void space saturation, and less than that found for amine to amide transformation (quantitative)[11] and organometallic compound impregnation.[20] Significantly longer reaction times (1 month with no apparent framework decomposition by pXRD and microanalysis) did not increase the conversion beyond a maximum of *ca.* 13%. Numerous attempts to increase the degree of amine functionalisation whilst maintaining framework integrity failed (different batches of IRMOF3, larger excess of salicylaldehyde, Dean–Stark reactions, heating to 60 °C and reflux). It is feasible that the framework decomposition observed under the forcing (reflux or Dean–Stark) reaction conditions occurs due to the formation of a significant H_2O concentration proximate to the Zn_4O cluster. The molecular species, 2-amino-terephthalic acid, on condensation with salicylaldehyde is completely converted to the respective salicylidene under forcing conditions.† Attempts to synthesize an IRMOF3-sal$_3$ framework utilising this preformed linker with $Zn(NO_3)_2$ in diethyl formamide under a range of conditions were repeatedly unsuccessful. In our hands, IRMOF3-sal$_x$ frameworks have to be made in a stepwise fashion, the incomplete conversion possibly attributable to an equilibrium position favouring amine and salicylaldehyde rather than salicylidene and H_2O.

To probe IRMOF3-sal$_{0.4}$ metal binding ability, V(O)acac$_2$·H_2O (acac = acetylacetonate) solutions (in dry CH_2Cl_2) were imbibed into IRMOF3-sal$_{0.4}$. V(O)acac$_2$ has the appropriate

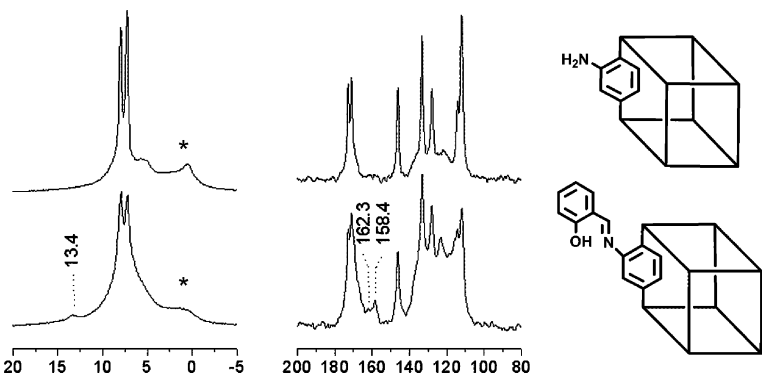

Fig. 2 Left, solid state ^{1}H MAS NMR spectra (30 kHz) and right, solid state ^{1}H–^{13}C CP/MAS NMR spectra (20 kHz) for IRMOF3 (top) and IRMOF3-sal$_{0.4}$ (bottom, materials were desolvated *in vacuo* at 1×10^{-3} torr, 80 °C, 18 h). The peaks at 162.3 and 158.4 ppm are in characteristic regions, assignable to the imine *C*=N and C_{aryl}–OH, respectively, * = impurity centred at 0.5 ppm we assign to residual toluene solvate and/or silicone grease.

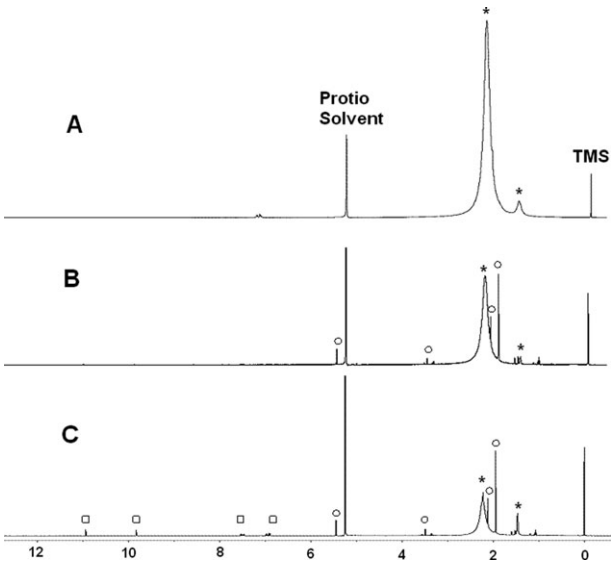

Fig. 3 ^{1}H NMR spectra of IRMOF3-sal$_{0.4}$ suspended in a CD_2Cl_2 solution of V(O)acac$_2$·H_2O. Spectra A: time zero; B: t = 2 days; C: t = 10 days. * = V(O)acac$_2$·H_2O resonances, ○ = resonances for the two tautomers of acetylacetone, □ = salicylaldehyde resonances.

dimensions to freely diffuse through the pore windows present in IRMOF3[20] (fixed pore window diameter of ~8 Å, approximate dimensions of V(O)acac$_2$ = 6.2 × 8.3 × 2.5 Å).[21] Furthermore control reactions established that IRMOF3 does not adsorb any detectable amounts of V(O)acac$_2$. V(O)acac$_2$ was imbibed into IRMOF3-sal$_{0.4}$ over 7 days (at 298 K) followed by repeated washing and subsequent evacuation, resulting in the formation of a material with empirical formula $(Zn_4O)(O_2C–C_6H_3(NH_2)–CO_2)_{2.6}(O_2C–C_6H_3(NC(H)-C_6H_4O–[V(O)acac])-CO_2)_{0.4}$, IRMOF3-Vsal$_{0.4}$. The exact composition of IRMOF3-Vsal$_{0.4}$ is determined by combined elemental, TG and EDX analysis, whilst comparable XRPD patterns for IRMOF3-Vsal$_{0.4}$ and IRMOF3 confirm the persistence of the extended open framework structure.† Pore void space decreases after vanadyl binding with less toluene guest solvent adsorbed further corroborating metal complexation.† The consistent 10 : 1 Zn : V molar ratio observed by EDX analysis for all crystallites precludes salicylidene formation as a minor amorphous impurity. IRMOF3-Vsal$_{0.4}$ is formed by the chemisorption of one V(O)acac$_2$ per framework salicylidene functionality. The failure to load V(O)acac$_2$ into IRMOF3 precludes complexation *via* the NH_2 functionality.

Solution-state ^{1}H NMR spectroscopy is highly informative for the analysis of soluble by-products from the loading procedure (Fig. 3). Initially the only observed resonance is the paramagnetically broadened CH_3 group of V(O)acac$_2$ and H_2O (Fig. 3A). On standing for several days new resonances appear and grow in intensity; these correspond to the two tautomers of acetylacetone (Fig. 3B). The detection of acetylacetone *exo*-framework confirms that the salicylidene moiety has protonated acac, displacing it from the coordination sphere of vanadium. Longer loading times increase the intensity of the acetylacetone resonances, but prolonged standing (>7 days) resulted in a slow growth of peaks corresponding to salicylaldehyde (Fig. 3C). This is attributed to additional H_2O (from V(O)acac$_2$·H_2O) shifting the equilibrium position, hydrolysing the imine. IRMOF3-sal$_{0.4}$ suspended in CD_2Cl_2 over the same time period evolved no salicylaldehyde.† This experiment in combination with the analytical data demonstrates that only the salicylidene moiety can bind vanadium.

A preliminary catalytic investigation revealed that IRMOF3-Vsal$_{0.4}$ is active for the oxidation of cyclohexene with ^{t}BuOOH (40% conversion of cyclohexene in THF at 60 °C for 72 h). Catalysis was shown to be unambiguously heterogeneous (filtered supernatant is inactive) but the poor turnover frequencies combined with loss of framework integrity (judged by XRPD) during the catalysis limits its applicability in this particular reaction. Nevertheless, IRMOF3-Vsal$_{0.4}$ is a rare example of a MOF with unsaturated metal centres immobilized on the pore surface. The observed catalysis does provide proof of principle that, *via* sequential functionalization, a porous MOF can be chemically transformed to introduce useful ligating groups (the salicylidene), activating the material towards metal complex binding and producing a catalytically active MOF. We emphasize that post-synthetic chemical transformation is integral to achieving catalyst heterogenization, with unfunctionalised starting material displaying no capacity for metal binding. Solid state NMR spectroscopy was shown to be a vital diagnostic technique for monitoring MOF functionalisation. In addition, the facile methodology introduced to improve the moisture tolerance of the IRMOF series is highly significant given the widespread use of these materials and the documented property repeatability issues arising from H_2O sensitivity.[16]

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