Electronic Supporting Information for

Framework Functionalisation triggers Metal Complex binding

Michael J. Ingleson, Jorge Perez Barrio, Jean-Baptiste Guilbaud, Yaroslav Z. Khimyak
and Matthew J. Rosseinsky*

Experimental Details:

Framework **IRMOF3 and MOF-5** were synthesised according to the published protocol.[1,2] Unless otherwise stated all other materials were used as received from commercial vendors. DMF, $CHCl_3$ and CH_2Cl_2 were dried and degassed using standard methodology and stored over activated molecular sieves under argon. Toluene used was standard analytical reagent grade with no drying techniques applied. Unless otherwise noted all procedures were carried out in air. Phase purity of starting IRMOF3 material was determined by a combination of powder X-ray Diffraction (pXRD) and desolvated microanalysis. Solid-state NMR spectra were measured on a Bruker Avance 400 DSX spectrometer operating at 100.61 MHz for ^{13}C and 400.13 MHz for ^{1}H. The values of chemical shift are referenced to TMS. 2.5 mm double resonance commercial probehead with zirconia rotors driven by air gas was used for the ^{1}H solid-state NMR spectroscopy and the ^{1}H-^{13}C CP/MAS NMR experiments. For the ^{1}H-^{13}C CP/MAS experiments, a ^{1}H $\pi/2$ pulse widths of 2.40 µs was used with 4.0 ms contact time and an optimised recycle time delay of 20.0 s. Two Pulse Phase modulation (TPPM) heteronuclear decoupling with was used during the acquisition with a ^{1}H *rf* decoupling field of *ca.* 100 kHz. MAS rate of 20.0 kHz was used. The ^{1}H MAS NMR spectra were recorded at a MAS rate of 30 kHz using a recycle time of 5.0 s and a rf field of *ca.* 100 kHz.

IRMOF3-tol$_x$: ($x \approx 5$, degree of solvation varies dependent on sample exposure time): following the standard synthetic activation utilising dry chloroform and inert atmosphere, the activated IRMOF3 materials was soaked in standard analytical reagent grade toluene (3 fresh portions, for 4 hours each). The material is filtered and stored under inert atmosphere. Alternatively, the material can be left in wet toluene for months with no decomposition and filtered prior to use. Phase purity is determined by xRPD. Predicted microanalysis for $(Zn_4O)(O_2C\text{-}C_6H_3(NH_2)\text{-}CO_2)_3(toluene)_{4.7}$: C = 54.7 %, H = 4.2 %, N = 3.3 %. Found C = 54.2 %, H = 4.4 % N = 3.1 %. Corresponds to a predicted 35 % solvent mass loss; observed mass loss by thermogravimetric analysis = 37 % before framework decomposition. Desolvated microanalysis, predicted: C = 35.4 %, H =1.9 %, N = 5.2 %, Found, C = 34.9 %, H = 2.1 % N = 5.1 %.

IRMOF3-sal$_{0.4}$: IRMOF3-tol$_5$ (0.25 g, 0.2 mmol based on empirical formula unit) was suspended in 5 ml of standard analytical grade toluene. Two equivalents (per NH_2 functionality, 1.2 mmol) of salicylaldehyde was added by microlitre syringe. After standing for seven days the crystallites had a noticeable yellow hue; the solution was then decanted and soaked (and solvent subsequently decanted) three times with aliquots (5 ml) of fresh toluene (soaking time of 18 hours). Desolvation *in-vacuo* (90°C, 24 hours, $1x10^{-3}$ torr) resulted in the isolation of the desolvated material, IRMOF$_3$-sal$_{0.4}$. Phase purity was determined by xRPD. Predicted microanalysis for $(Zn_4O)(O_2C\text{-}C_6H_3(NH_2)\text{-}CO_2)_{2.6}(O_2C\text{-}C_6H_3\text{-}(N{=}C(H)C_6H_4OH)\text{-}CO_2)_{0.4}$: C = 37.6 % H = 2.0 % N = 4.9 %. Found: C = 37.8 %, H = 2.1 %, N = 4.9 %. Yield based on amine conversion is 13%.

Shorter loading: An identical procedure to that followed for the synthesis of IRMOF3-sal$_{0.4}$ except washing commenced after 4 days. This yielded a phase pure material (by pXRD) that microanalysis revealed had a empirical formula of $(Zn_4O)(O_2C\text{-}C_6H_3(NH_2)\text{-}$

$CO_2)_{2.75}(O_2C$-C_6H_3-$(N{=}C(H)C_6H_4OH)$-$CO_2)_{0.25}$. Predicted: C = 36.8 %, H = 1.9 % N = 5.0 %. Found C = 36.7, H = 1.8 % and N = 5.0 %. This corresponds to an 8 % amine conversion.

Test loading of Salicylaldehyde into MOF-5

MOF-5-tol$_x$ (0.03g) was suspended in 10 ml of toluene. Approximately three equivalents ($7.3\mathrm{x}10^{-5}$mol, 0.009g) of salicylaldehyde was added and the sample sealed. After standing for 7 days the sample was washed in an identical manner to that described for IRMOF3-sal$_{0.4}$ and desolvated *in-vacuo*.

MOF-5 desolvated before attempted salicylaldehyde loading, predicted for $(Zn_4O)(O_2C$-C_6H_4-$CO_2)_3$: C = 37.4 %, H = 1.6 % N = 0 %. Found C = 37.3 H = 1.6 N = 0.

After attempted salicylaldehyde loading C = 37.2 %, H = 1.5 % N = 0 %.

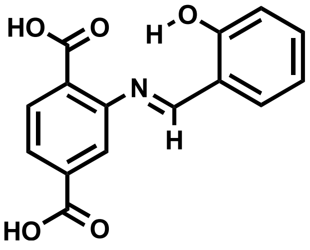
IRMOF3-Vsal$_{0.4}$: This procedure was performed utilizing dried solvent under inert atmosphere using standard Schlenk techniques. Desolvated IRMOF3-sal$_{0.4}$ (0.03g, $3.5\mathrm{x}10^{-5}$ mol per empirical formula unit corresponding to $1.4\mathrm{x}10^{-5}$ mol if salicylidene units) is suspended in CH_2Cl_2 (5 ml), 37mgs ($1.4\mathrm{x}10^{-4}$ mol, 10 equivalents per salicylidene unit) is dissolved in dry CH_2Cl_2 and added via cannula under inert atmosphere. The turquoise solution with yellow solid is allowed to stand for seven days before the solution is decanted and the solid soaked in fresh dry CH_2Cl_2 (10 ml aliquots overnight each). The material was phase pure by pXRD. Desolvation resulted in the successful isolation of IRMOF3-Vsal$_{0.4}$, predicted desolvated microanalysis for $(Zn_4O)(O_2C$-$C_6H_3(NH_2)$-$CO_2)_{2.6}(O_2C$-C_6H_3-$(N{=}C(H)C_6H_4O)$-$CO_2)_{0.4}(V(O)acac)_{0.4}$: C = 37.5 % H = 2.1 % N = 4.6 %. Found: C = 37.6, H = 2.2 %, N = 4.6 %.

Bulk metal ratio (by ICP on a sample exposed to atmosphere, therefore unknown degree of H_2O uptake invalidating exact percentage composition analysis actual values recorded V = 2.1 %, Zn = 24.0 %) expected molar ratio 10 Zn : 1 V found 9.0 Zn : 1 V.

Test loading of V(O)acac$_2$ into IRMOF3 unfunctionalised:

This procedure was performed utilizing dried solvent under inert atmosphere using standard Schlenk techniques. IRMOF3-tol$_5$ was loaded into a Schlenk flask and desolvated (*invacuo* 18 hours, 90°C, $1\mathrm{x}10^{-3}$ torr). 30 mgs of V(O)acac$_2$ was dissolved in 5 ml dry CH_2Cl_2 and added by cannula to IRMOF3-tol$_5$. The mixture was allowed to stand for 7 days followed by analogous CH_2Cl_2 washing to that reported above. Dissolution of the solid material and metal content analysis by ICP revealed only trace vanadium content < 0.1 %. Furthermore EDX on 10 random crystallites confirmed no significant V presence.

Synthesis of 2-salicylidene-terephthalic acid



2-amino-terephthalic acid (0.20g 11mmol) was dissolved in EtOH and 1 equivalent of salicylaldehyde (11mol, 1.21 ml) added. After refluxing for 4 hours an insoluble orange-yellow precipitate has formed, which is filtered, washed with EtOH (x2) and dried.
IR (cm^{-1}) KBr: C=N 1693cm^{-1}.
Predicted microanalysis for $C_{15}N_1O_5H_{11}$: C = 63.2 %, H = 3.9 %, N = 4.9 %, Found C = 63.3 %, H = 4.0 %, N = 4.9 %.
^{1}H NMR (d_6-DMSO): 13.32 (br, 2H, CO_2*H),* 8.98 (br, 1H, Aryl-OH hydrogen bonded to imine N), 7.95 – 7.68 (overlapping multiplets, 4H, aryl and *(H)*C=N), 7.4 (m, aryl 2H) and 6.98 (m, aryl 2H)

Attempted Framework formation reactions with 2-salicylidene-terephthalic acid:
A range of conditions were tried combining $Zn(NO_3)_2.6H_2O$ and 2-salicylidene-terephthalic acid in dry DEF. Variables altered including, concentration, respective ratio, temperature and reaction time. All yielded no insoluble crystalline phases.

Catalysis:
These were performed utilizing dried solvent under inert atmosphere using standard Schlenk techniques. Before catalysis was attempted the stability of IRMOF3 with respect to the reagents was examined. IRMOF3-tol_5 was desolvated, suspended in dry THF (10 ml), then 0.1ml of cyclohexene and 50μl of ^{t}BuOOH were added by microlitre syring. The sample was sealed under inert atmosphere and left for 20 hours. The isolated supernatant revealed no catalysis (cyclohexene was returned unreacted by analysis using an Alltech EC-1 boiling point column). Importantly pXRD revealed the material after exposure to the catalysis reagents (^{t}BuOOH and cyclohexene) remained crystalline and phase pure.
A similar catalysis procedure to that previously reported for heterogenised vanadyl catalysts was followed.[3] In a typical reaction 10 mgs of desolvated IRMOF3-$VSal_{0.4}$ was loaded into a Youngs tube in a glove box. 5 ml of the desired (dried/degassed) solvent was added and 30μl of cyclohexene. 1.5 equivalents of ^{t}BuOOH (per cyclohexene) was added (as a 5.5M solution in decanes) and the sample stirred for the desired length of time and at the desired temperature. Post catalysis the samples were filtered, the filtrate concentrated and used for GC analysis whilst the solid is rapidly immersed in toluene to generate the stabler guest exchanged species, subsequently filtered and used for pXRD analysis.

1 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**.
2 J. L. C. Roswell and O. M. Yaghi, *J. Am. Chem. Soc*, 2006, **128**, 1304.
3 M. Salavati-Niasari, M.R. Elzami, M. R. Mansournia and S. Hydarzadeh, Journal of Molecular Catalysis A: Chemical 221 (2004) 169-175

Figure S1: Key for schematic representation of IRMOF3. Left simplified schematic of IRMOF3, right atomic representation of the schematic, which defines one cavity (encapsulated by 12 amino-terephthalate edges and eight Zn_4O corners). Only one of the disordered nitrogen positions is shown arbitrarily for clarity.

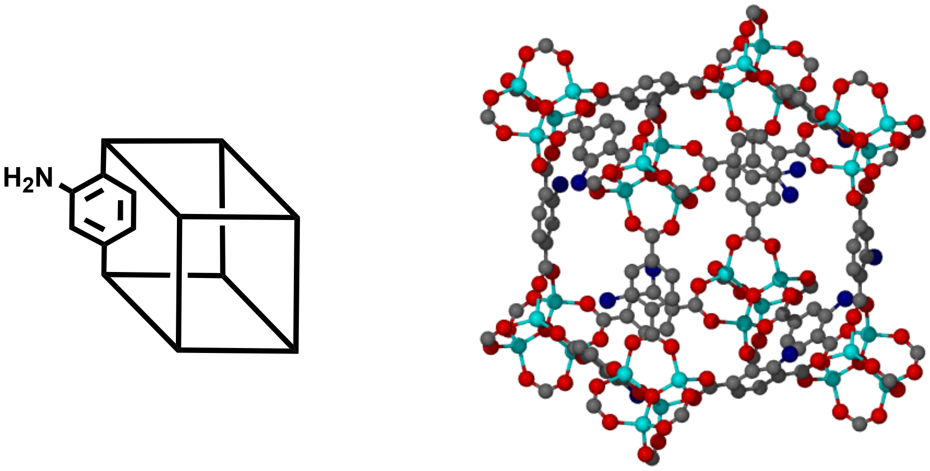


Figure S2:
Solid state UV/Vis spectra for IRMOF3-tol$_x$ and IRMOF3-sal$_{0.4}$ solvated (i.e. with toluene guest molecules)

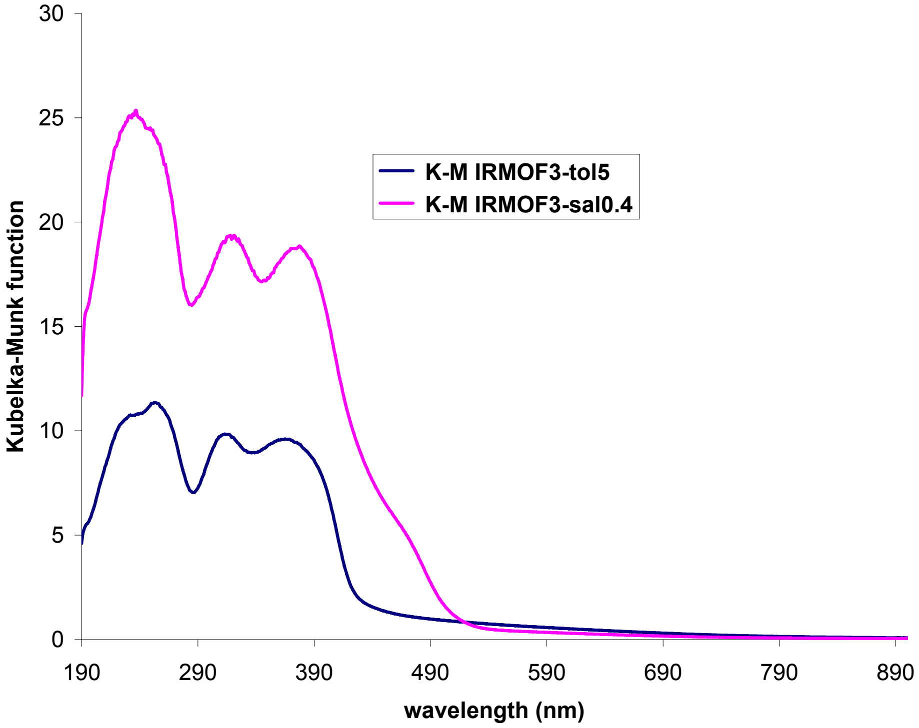


FIGURE S3:
Gas adsorption isotherms (CO_2, 195 K) for IRMOF3 and IRMOF3-sal$_{0.4}$

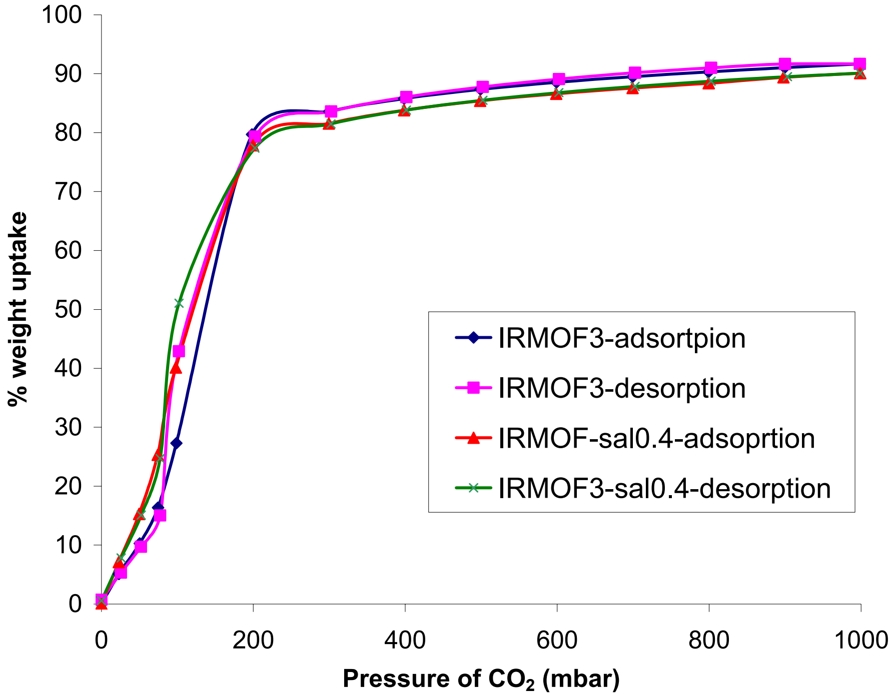


FIGURE S4: expanded from 200mbar to 1000mbar for CO_2 gas adsorption (195 K) for IRMOF3 and IRMOF3-sal$_{0.4}$

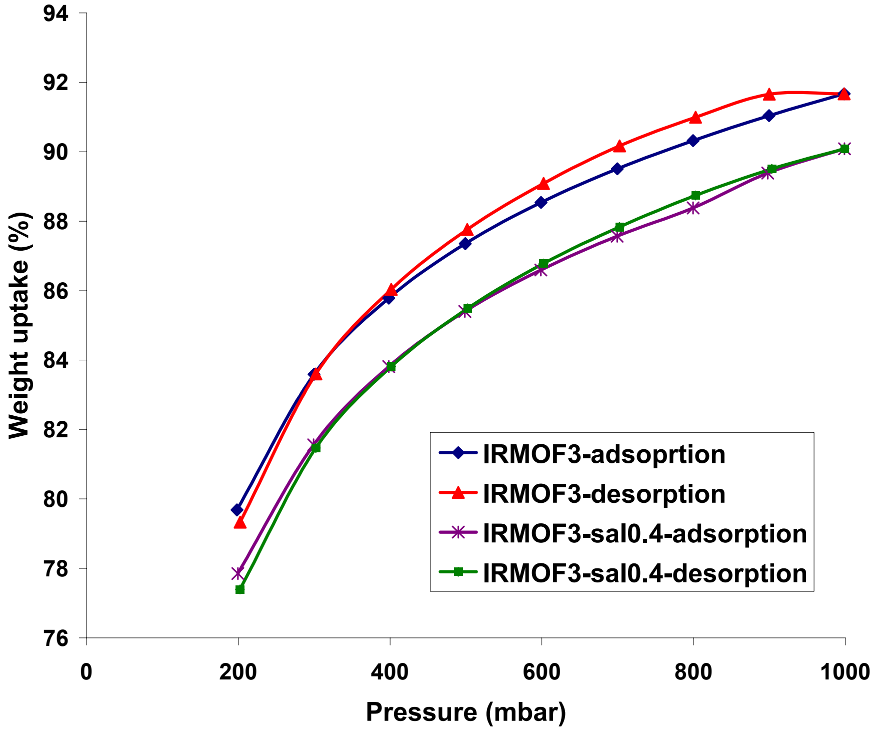


FIGURE S5: CO_2 gas adsorption isotherms (195K) for fresh IRMOF3 and IRMOF3 after storing immersed in standard analytical grade toluene for 3 months

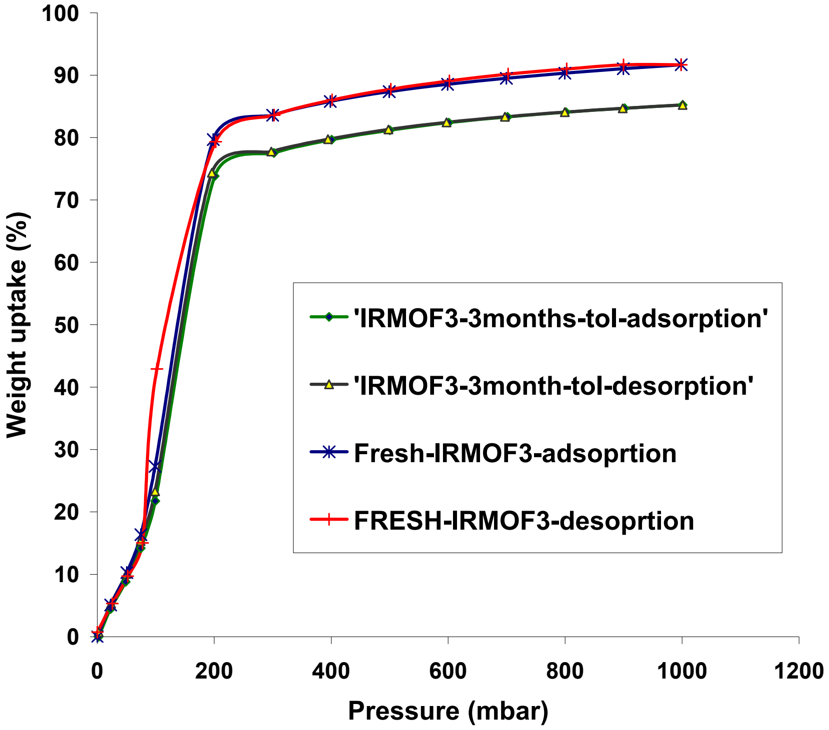
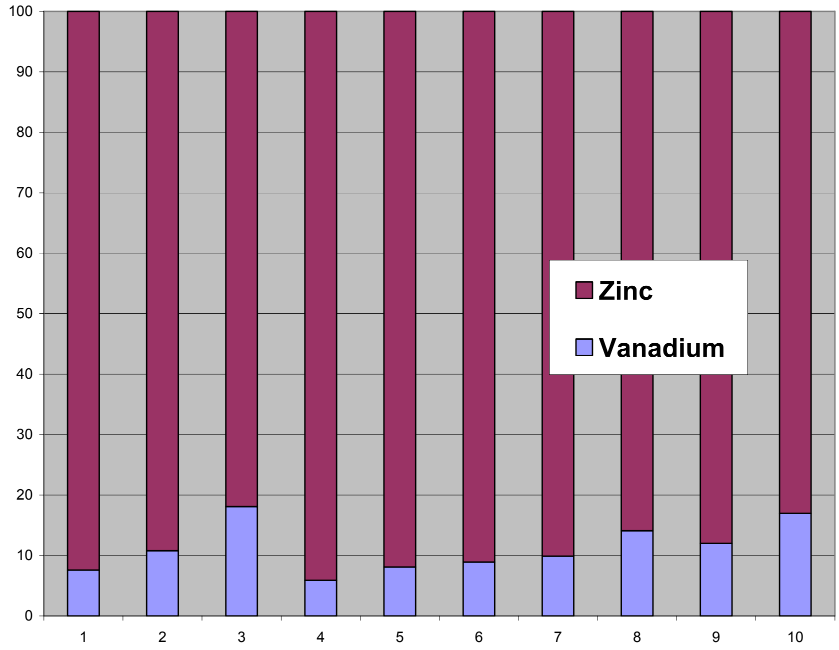
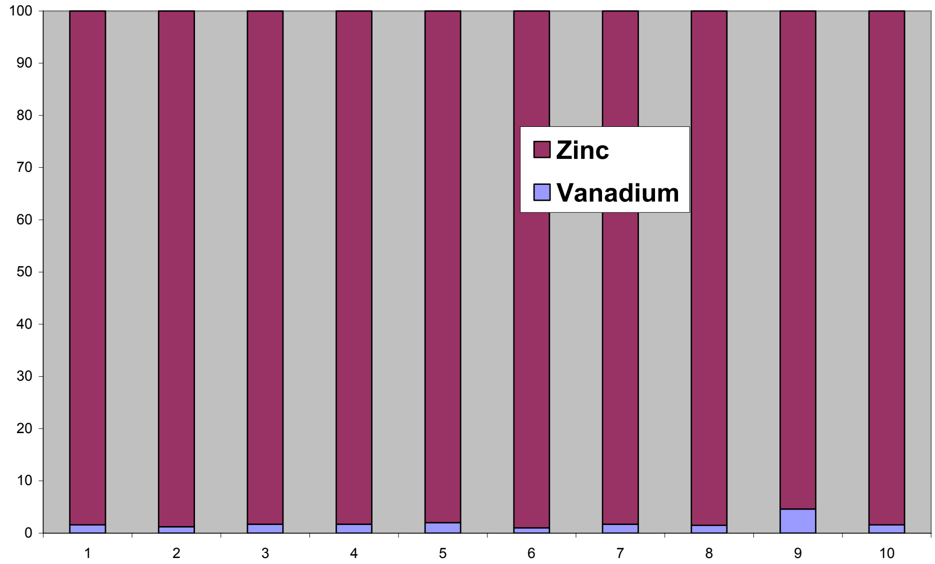


FIGURE S6 EDX Analysis for IRMOF3-Vsal$_{0.4}$:



Average molar ratio of 89 : 11 (Zn : V). The observed variation is presumably due to a small statistical variation in the salicylidene groups per crystallite.

FIGURE S7: EDX Analysis for attempted loading of V(O)acac$_2$ into IRMOF3.



Effectively zero V present (considering an error of +/- 2 %). A molar ratio of 98 : 2 (Zn : V)

FIGURE S8: TGA for toluene solvated IRMOF3 (37% solvent weight loss)

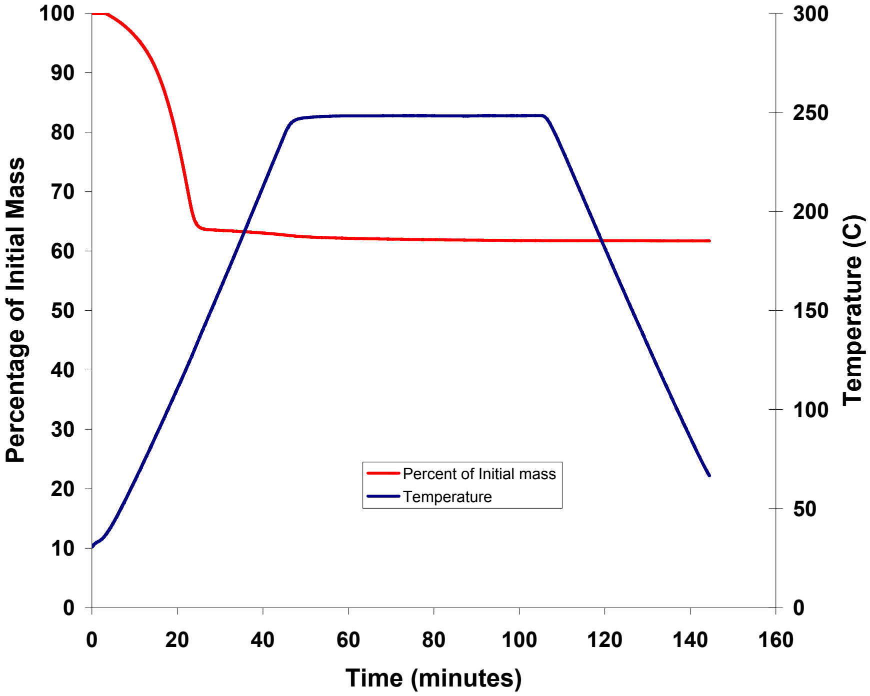


FIGURE S9: TGA for toluene loaded IRMOF3-Sal$_{0.4}$ (33.2% solvent weight loss)

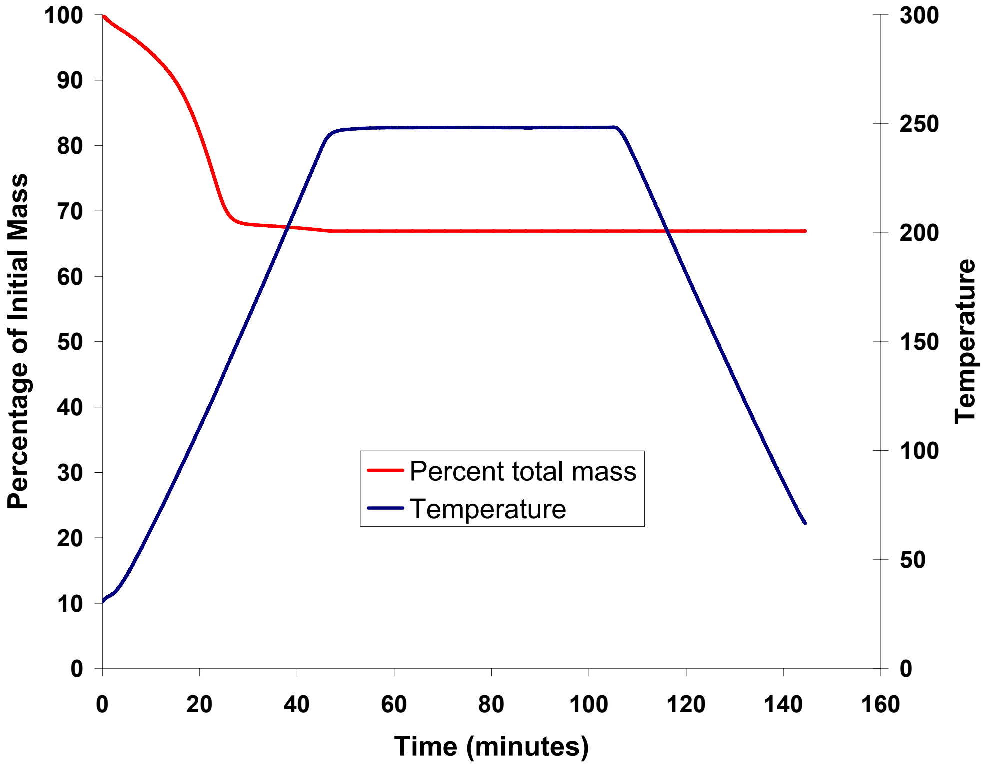


FIGURE S10:TGA for toluene loaded IRMOF3-Vsal$_{0.4}$ (30 % solvent weight loss)

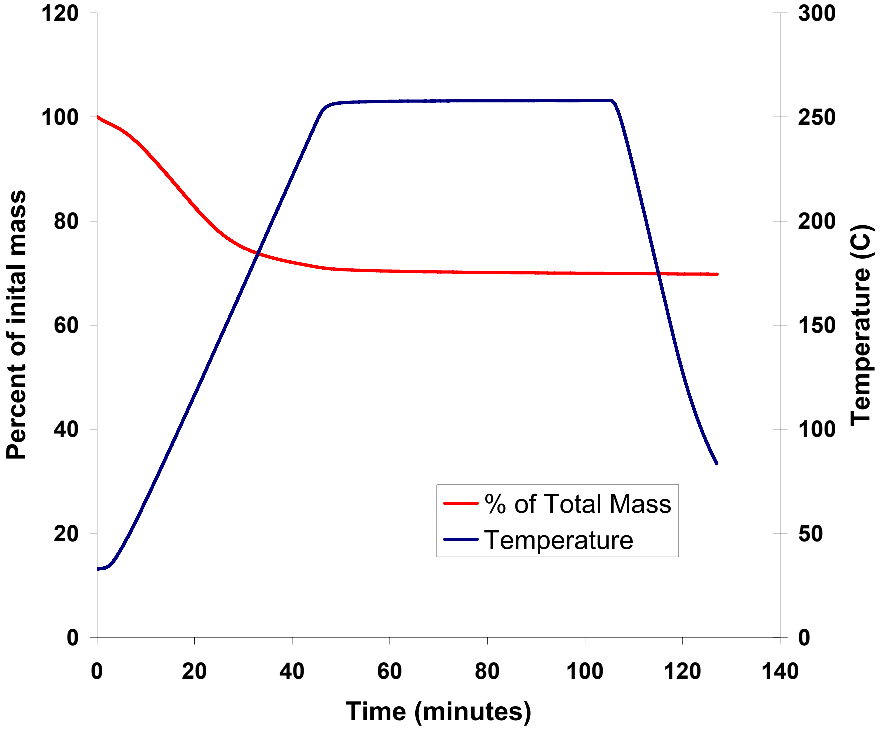


FIGURE S11: Overlay of the three solvent weight losses (by TGA) from each of the above materials material

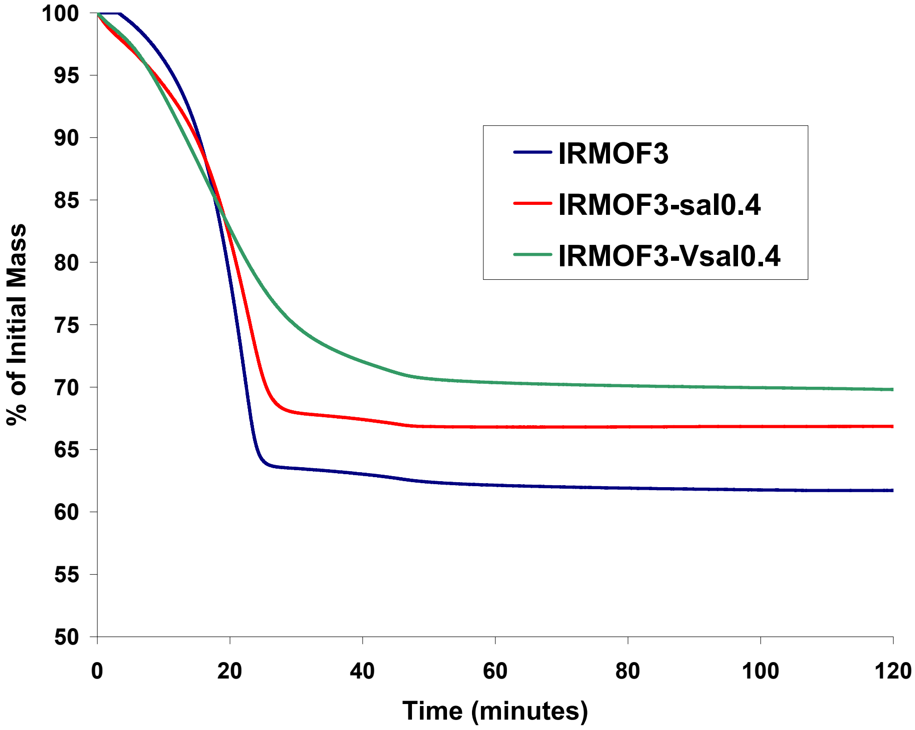


Figure S12:
pXRD patterns for IRMOF3 collected immediately after immersion in toluene, and after 3 months immersed in standard analytical grade toluene.

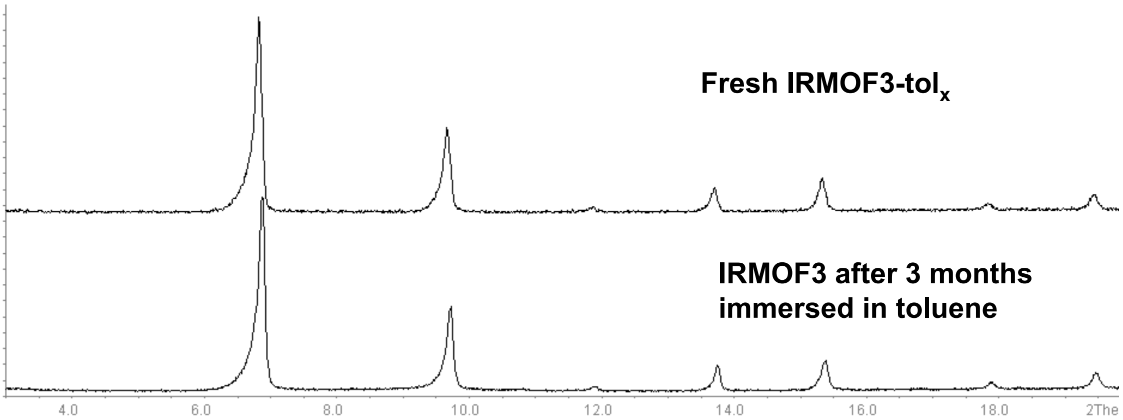


FIGURE S13: pXRD patterns for MOF-5 collected immediately after immersion in toluene, and after 3 months immersed in standard analytical grade toluene.

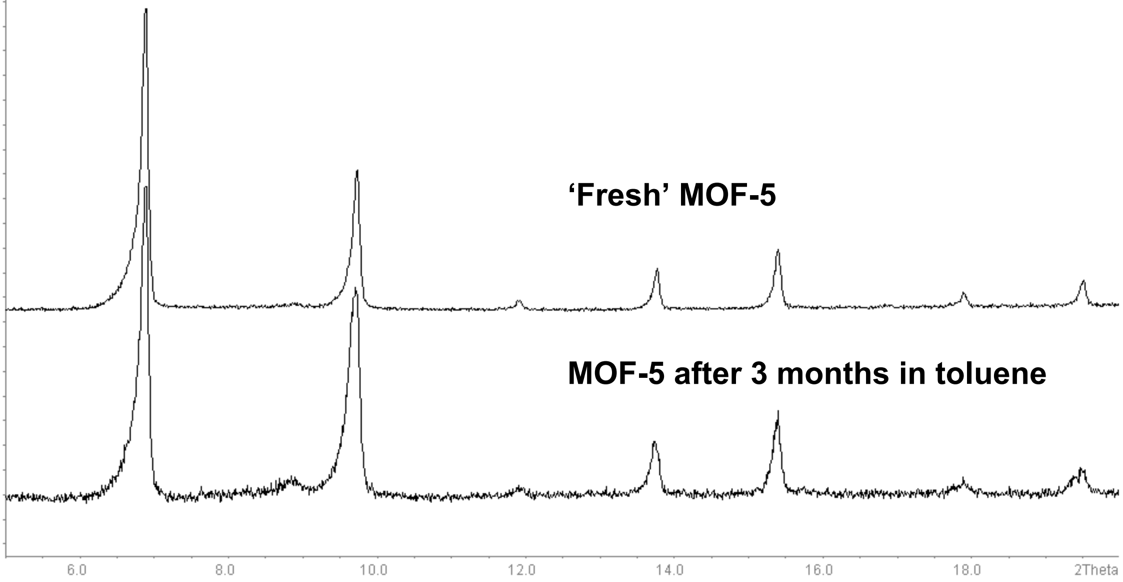


FIGURE S14:
Control solution-state ^{1}H NMR reaction. IRMOF3-sal$_{0.4}$ suspended in CD_2Cl_2