Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Information

Top-down Patterning of Zeolitic Imidazolate Framework Composite Thin Films by deep X-ray Lithography

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S.1 Experimental Detail

ZIF-9 was prepared in bulk powder form by dissolving 133.3 g $Co(NO_3)_2.6H_2O$ (Sigma-Aldrich) and 400 g PhIM (Koch-Light) in 4L of dimethylformamide (DMF) (Merck) at room temperature (molar ratio $Co(NO_3)_2.6H_2O$: PhIM : DMF = 1 : 7.39 : 113) and heating the solution to 130°C for 48 hrs. The solution was left to cool down naturally and collected by vacuum filtration overnight. The resulting purple powder was solvent-exchanged with dry methanol under a nitrogen atmosphere twice to remove entrained DMF and filtered and dried under vacuum to obtain 14.3 g of powder. Approximately 1 g of this powder was taken and milled using a mortar and pestle for subsequent experiments.

Lithography experiments were conducted using the Deep X-Ray Lithography (DXRL) beamline at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy). Samples were exposed to X-rays through a micropatterned mask. X-ray doses of 2165 J cm^{-2} at the top surface were used for the patterning process with a total exposure time of 1186 s. Samples were then gently rinsed post-exposure with ethanol and gently dried with compressed air.

XRD patterns were collected using a Bruker GADDS X-ray diffractometer using Cu Kα radiation with a 0.020° step size at 71.6 s per step.

Gas sorption analysis was conducted on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosimetry System using an ice bath to maintain the sample temperature at 273K.

SEM imaging was performed with a Zeiss Supra 40 instrument (Carl Zeiss MicroImaging GmbH, Germany) using secondary electrons as measuring signal, equipped with an EDX (Energy dispersive X-ray spectroscopy) system (EDAX Inc., NY) with a nominal resolution of 140 eV.

FTIR images were acquired using a Bruker Hyperion 3000 Vis–IR coupled with a Bruker Vertex 70 interferometer in reflection mode utilising a Focal Plane Array (FPA) detector to produce a 64 pixel x 64 pixel 2D chemical map of the surface, averaging 64 scans per point.

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S.2 Optical Microscope Images

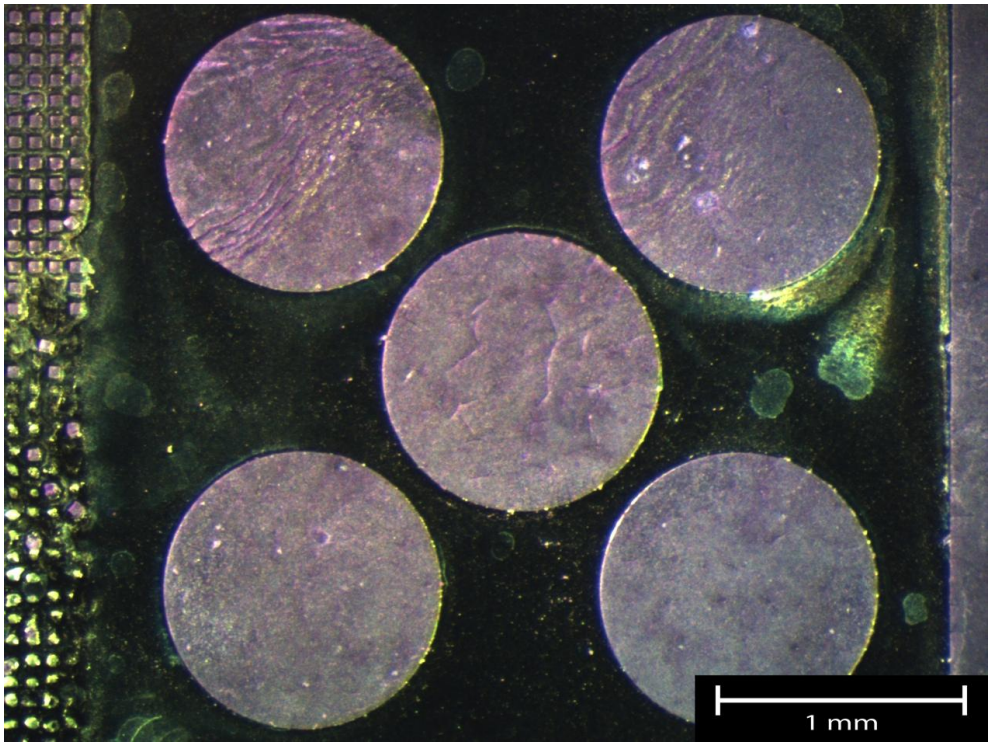

Fig S.1 – ~1mm features of ZIF-9/PhTES film on silicon wafer. Square pillars presented in paper are evident to the left; some have been subjected to excessive force during rinsing and have detached from the silicon wafer surface.

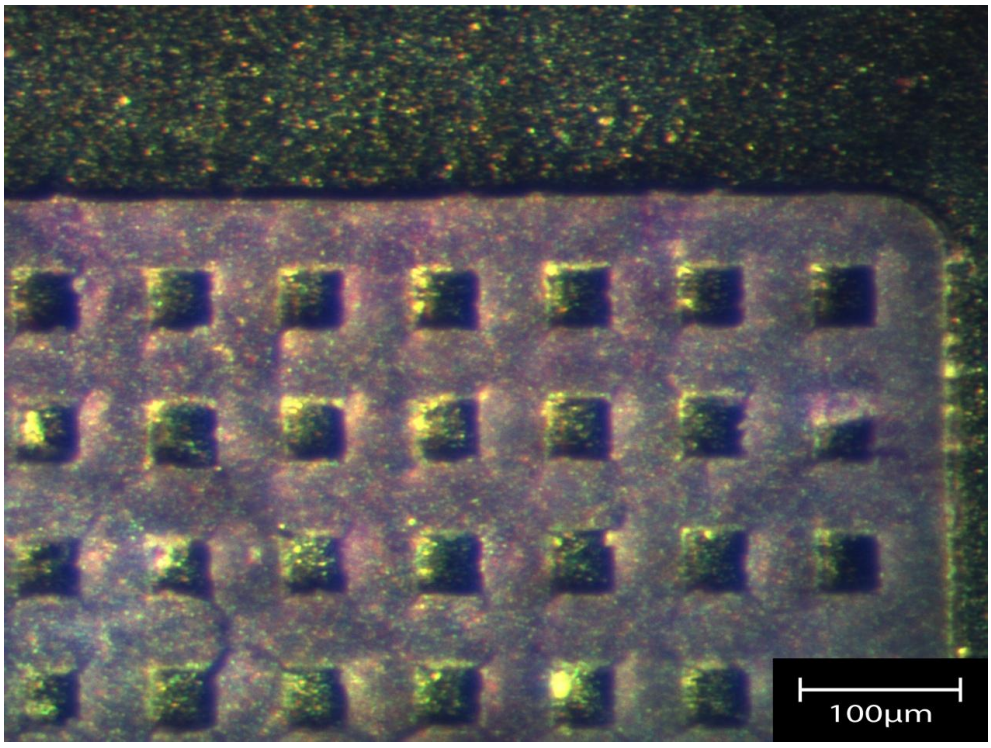

Fig S.2 - ~50µm square gaps etched away from an exposed film.

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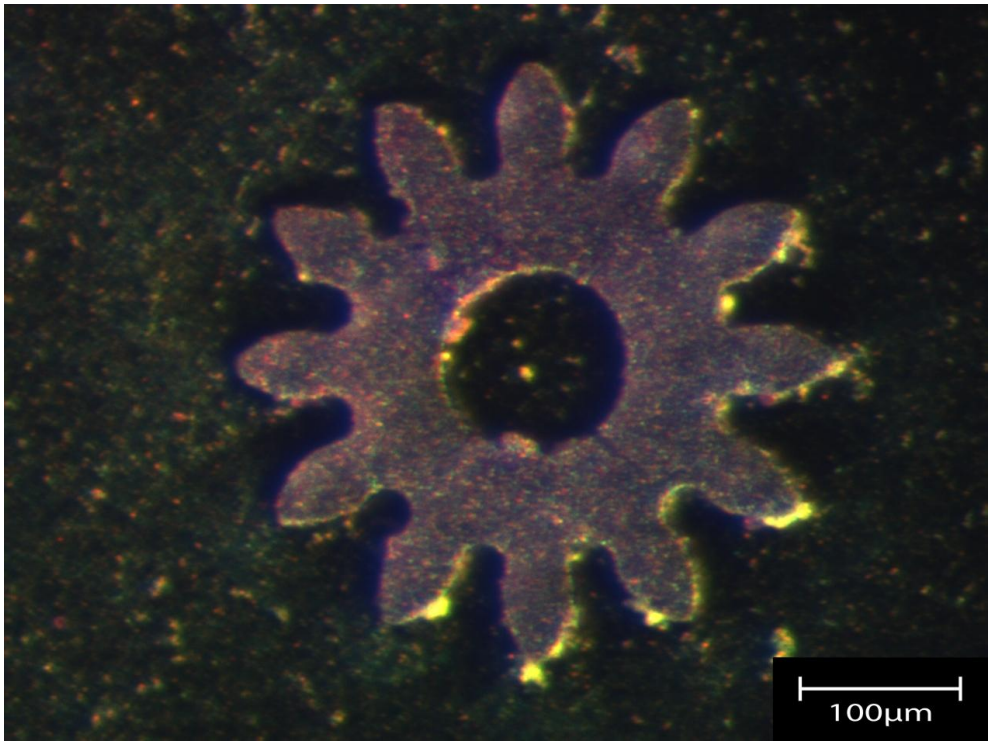

Fig S.3 - ~250µm microgear of ZIF-9/PhTES with sharp edge definition.

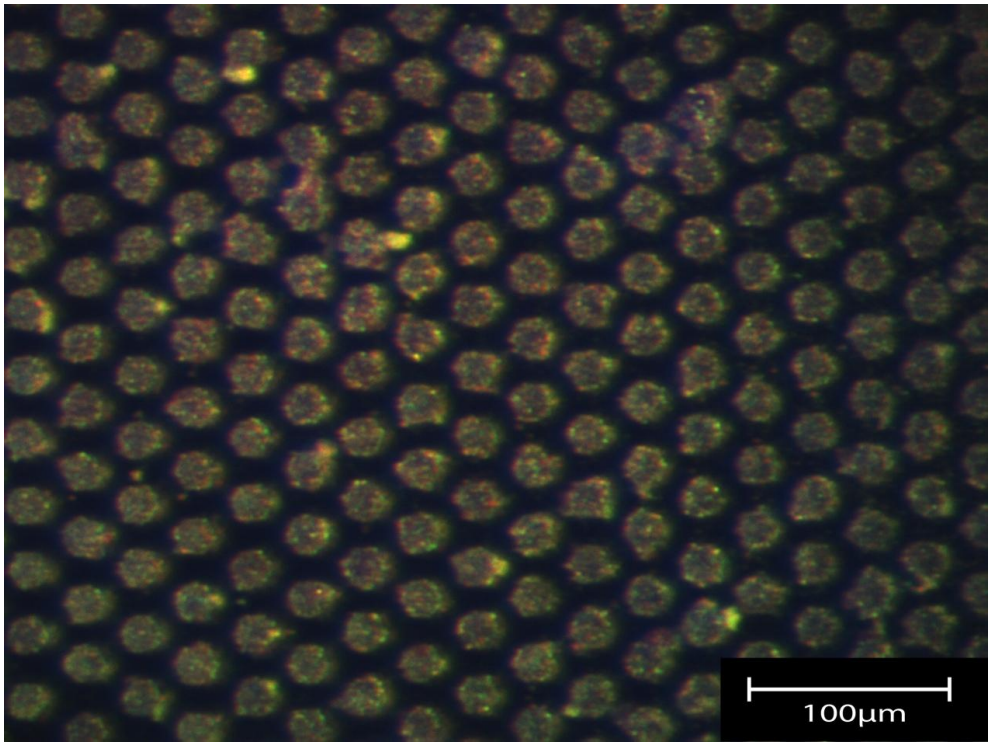

Fig S.4 - ~25µm hexagonal pillars of ZIF-9/PhTES.

S.3 SEM Images

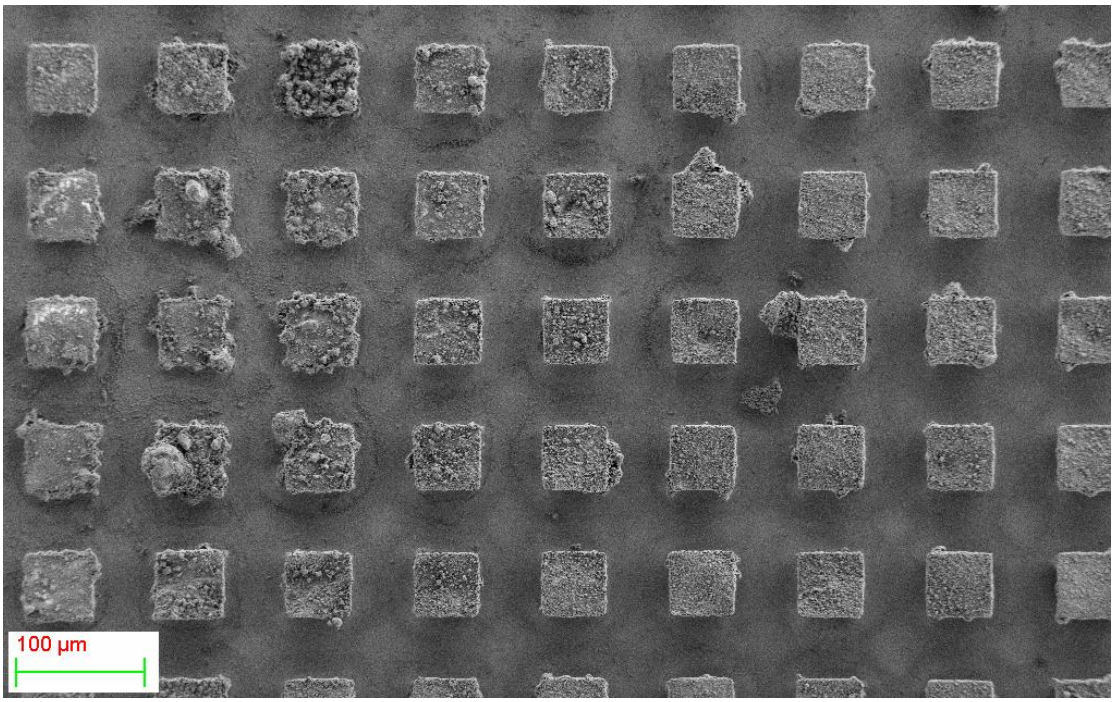

Fig S.5 – Imaging of 50µm x 50µm pillars showing surface roughness from ZIF-9 agglomeration.

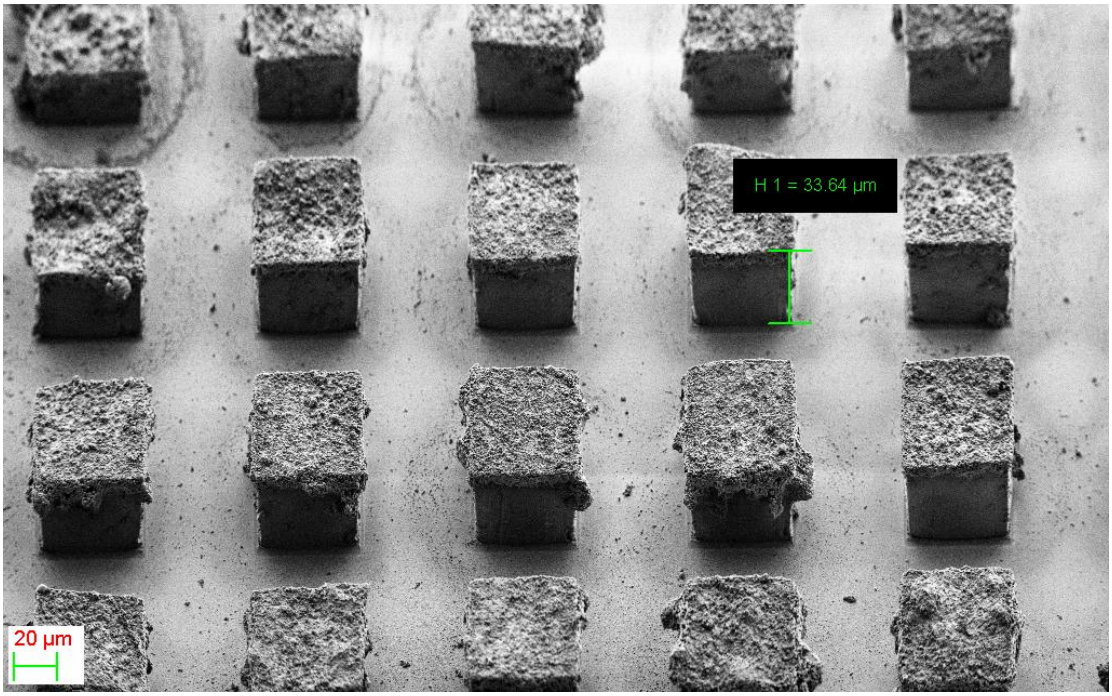

Fig S.6 – Imaging of ZIF-9/PhTES pillars from a 45° angle, showing height of film as 33.64µm.

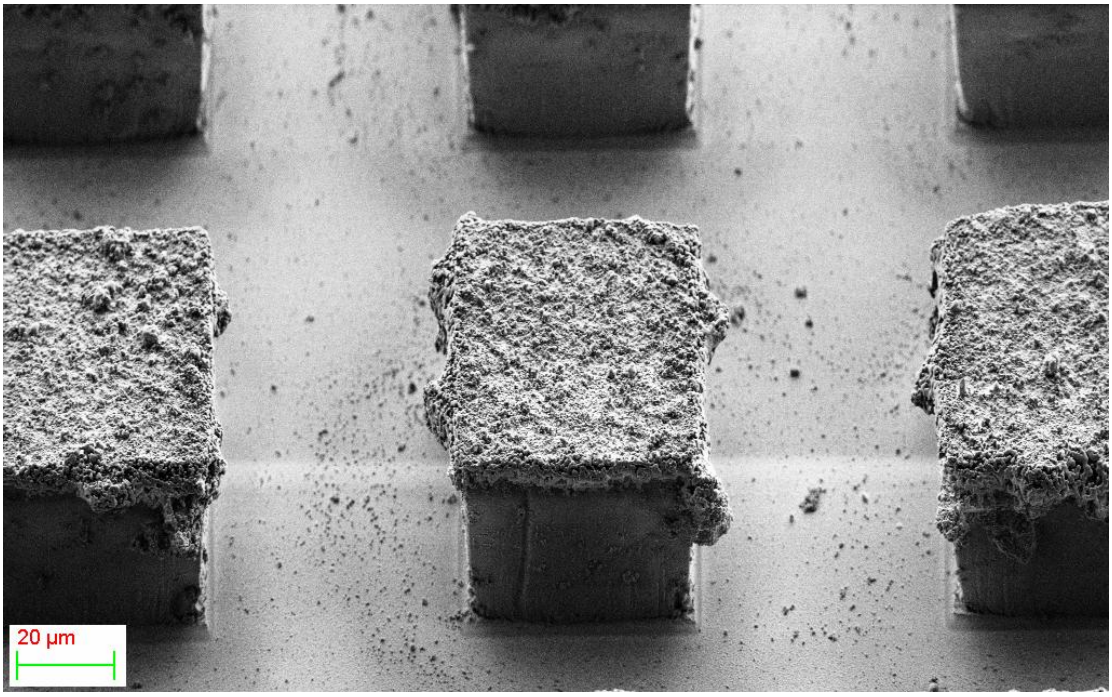

Fig S.7 – Close-up of ZIF-9/PhTES pillar at 45° angle emphasising sharp definition of edges of PhTES region due to X-ray exposure.

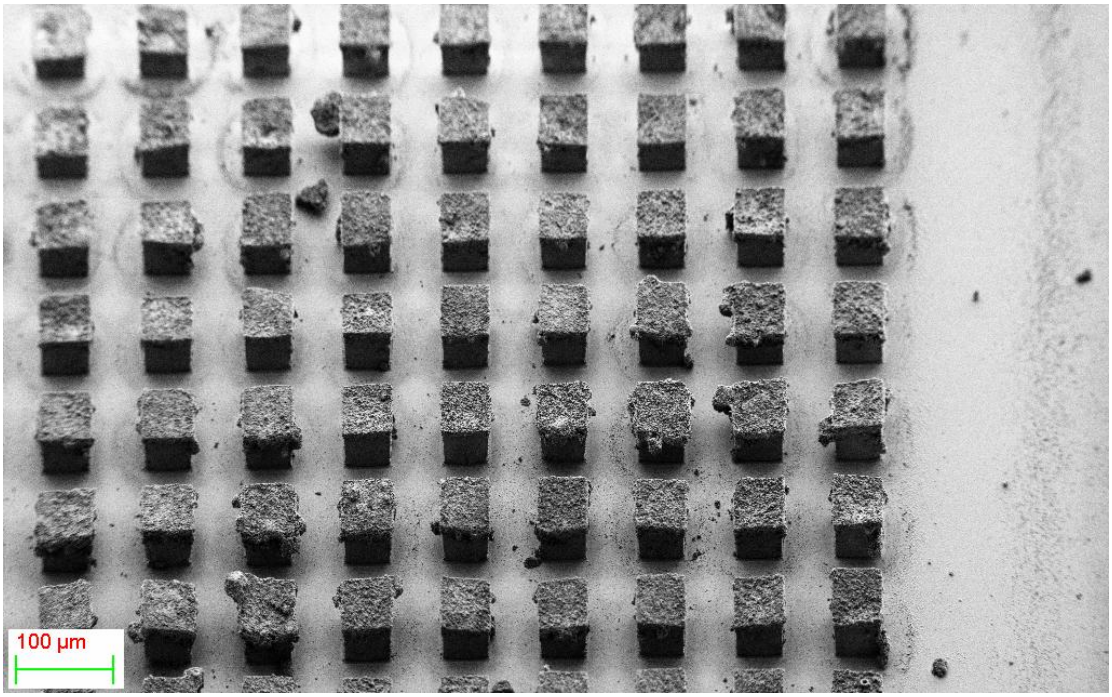

Fig S.8 – Additional wide view of regular pillar arrangement at 45° angle, showing some agglomeration of ZIF-9 not entirely rinsed away.

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S.4 X-Ray Diffraction Patterns

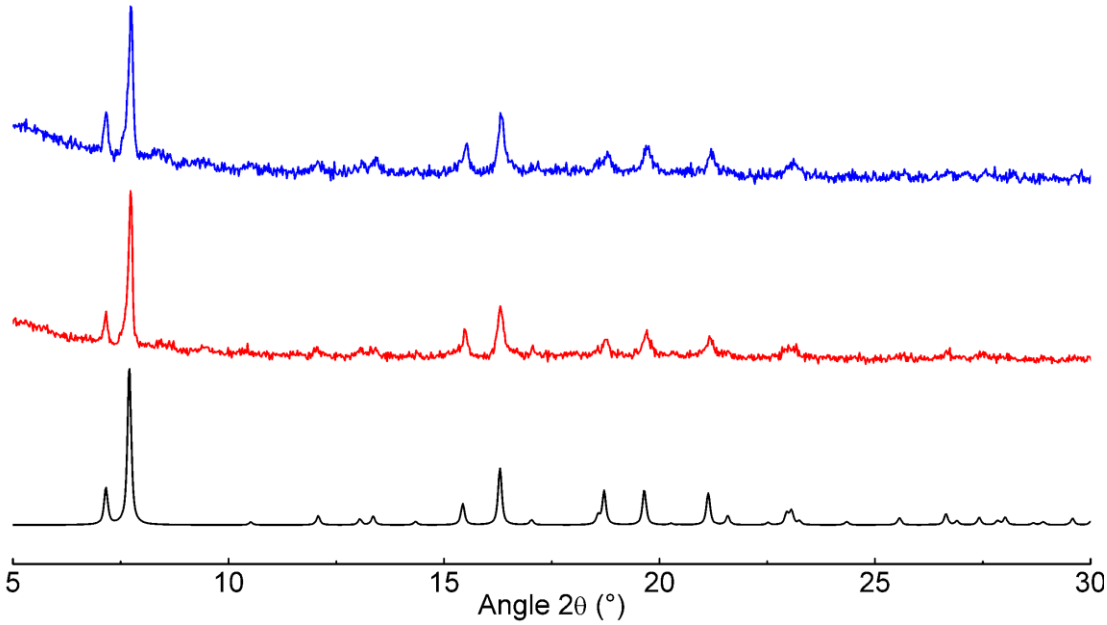

Fig S.9 – Powder XRD experiments show no difference between irradiated ZIF-9 (blue, top) and as-synthesised ZIF-9 (red, middle) as the structure and powder pattern predicted by theory (black, bottom) is maintained.

S.5 FTIR Data

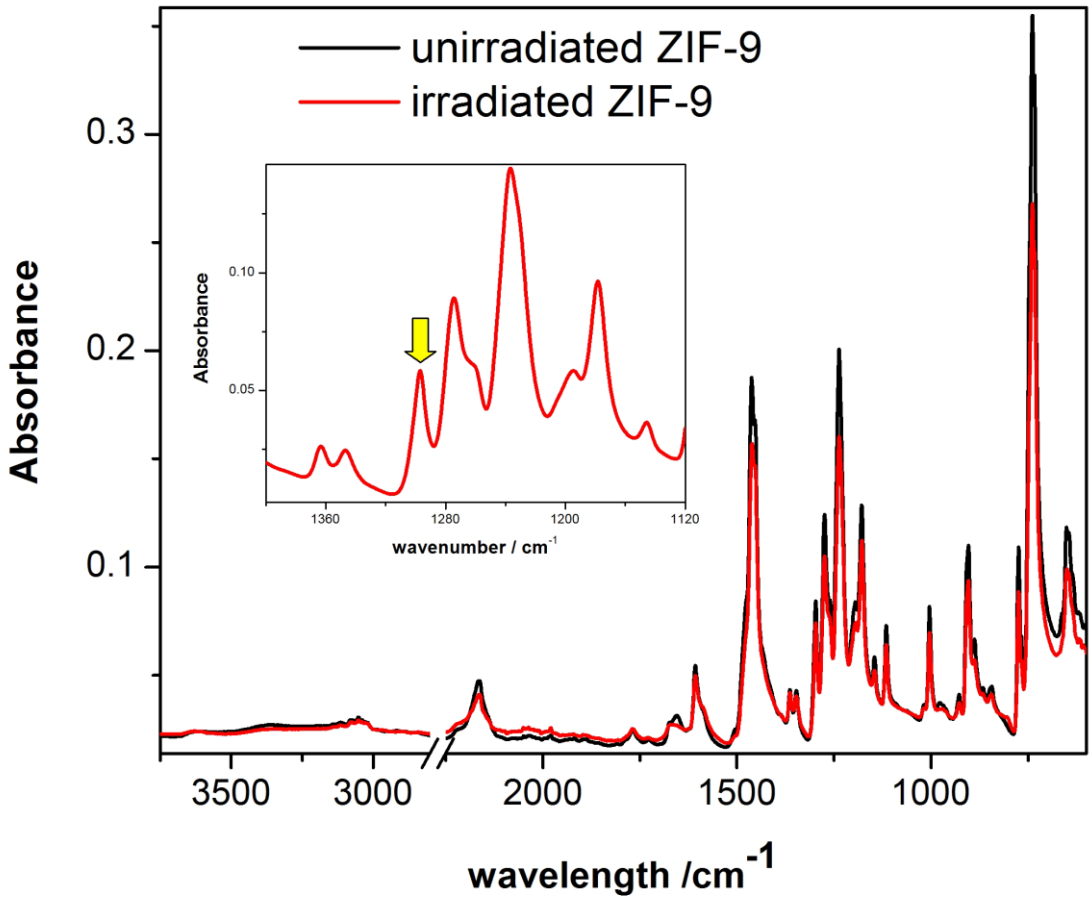

Fig S.10 – FTIR comparison of unirradiated and irradiated ZIF-9 powder showing little chemical change through X-ray exposure. The peak that was integrated over the imaged surface to generate **Fig. 3d** is indicated by the yellow arrow (inset).

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Table S.1 – Peak assignments for recorded powder ZIF-9 FTIR spectra in **Fig S.10** above. Calculated frequencies from reference data for benzimidazole were used for peak assignments.[1] Peak signal strengths are also reported (vs = very strong; s = strong; m = medium; w = weak; vw = very weak).

Observed Frequency (cm^{-1})	**Calculated Frequency (cm^{-1})** [1]	**Assignment** [1]
650 m	628	C-C-C in-plane bending
739 vs	739	C-H out-of-plane bending
774 m	774	C-H out-of-plane bending
844 vw	827	C-C ring breathing mode
888 w	881	C-H out-of-plane bending
904 m	906	C-H out-of-plane bending
1004 m	1012	C-C-C trigonal bending
1116 m	1130	C-H in-plane bending
1146 w	1146	C-H in-plane bending
1179 m	1185	C-H in-plane bending
1237 s	1241	C-C stretching
1275 m	1265	C-H in-plane bending
1297 m	1308	C-N stretching
1347 w	1352	C-N stretching
1363 w	1358	C-N stretching
1454 s	1449	C=C stretching
1462 s	1471	C=C stretching
1607 w	1619	C=C stretching

1. S. Mohan, N. Sundaraganesan and J. Mink, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 1991, 47, 1111-1115.