Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Probing Time Dependent Phase Transformation in a Flexible Metal-Organic Framework with Nanoindentation

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S1. Experimental Section

S1.1. Reagents and Solvents

The reagents and solvents employed in the synthesis were available commercially and are used in the as received condition without further purification. 1,4-naphthalenedicarboxylic acid (1,4-NDCH$_2$), 1,2-bis(4-pyridyl)ethane (1,2-BPE) and Zn(NO$_3$)$_2$·6H$_2$O were obtained from the Aldrich Chemical Company.

S1.2. Physical Measurements

Elemental analyses were carried out using a Flash 2000 Elemental Analyzer. IR spectrum of the compound was recorded on a Bruker IFS 66v/S spectrophotometer using KBr pellets in the region of 4000–400 cm^{-1}.

S1.3. Powder X-ray diffraction measurements

Powder X-ray diffraction (PXRD) pattern in different state of the samples were recorded on a PANalytical X'Pert PRO instrument with Bragg−Brentano geometry. Intensity data were recorded using an X'Celerator detector with 2θ range from 5–40° using Cu$_{K\alpha}$ radiation.

S1.4. Synthesis of Zn-MOF-1

The metal solution was prepared by dissolving Zn(NO$_3$)$_2$·6H$_2$O (0.5 mmol, 0.149 g) in 15 mL methanol in a beaker. In another beaker organic linkers 1,4-NDC (0.5 mmol, 0.108 g) and 1,2-bpe (0.25 mmol, 0.046 g) were mixed in DMF (2 mL) and 2-methoxyethanol (13 mL) to prepare the ligand solution. The metal and ligand solutions were then mixed slowly to avoid precipitation. The mixture was then filtered to remove any particles and then transferred to small 10 mL glass vials. The glass vials were then tightly capped and immersed in an oil bath that was already kept at 75 °C. The reaction mixture was left undisturbed for crystal growth. After 48 hours, colourless block shaped crystals of **Zn-MOF-1** was observed settled on the wall of the glass vials. These crystals were further used for characterization and nanoindentation purpose. A yield of 79%, relative to Zn, was obtained. Elemental analysis calculated for dried **Zn-MOF-1**, $C_{18}H_{12}NO_4Zn$, is as following: C 58.17, H 3.25, N 3.77; Observed: C 58.01, H 3.37, N 3.42. FT-IR (ATR, 500-4000 cm^{-1}): ν_{Ar}(C-H)=3060; ν_{as}(OCO)=1614; ν_{s}(OCO)=1369 cm^{-1}.

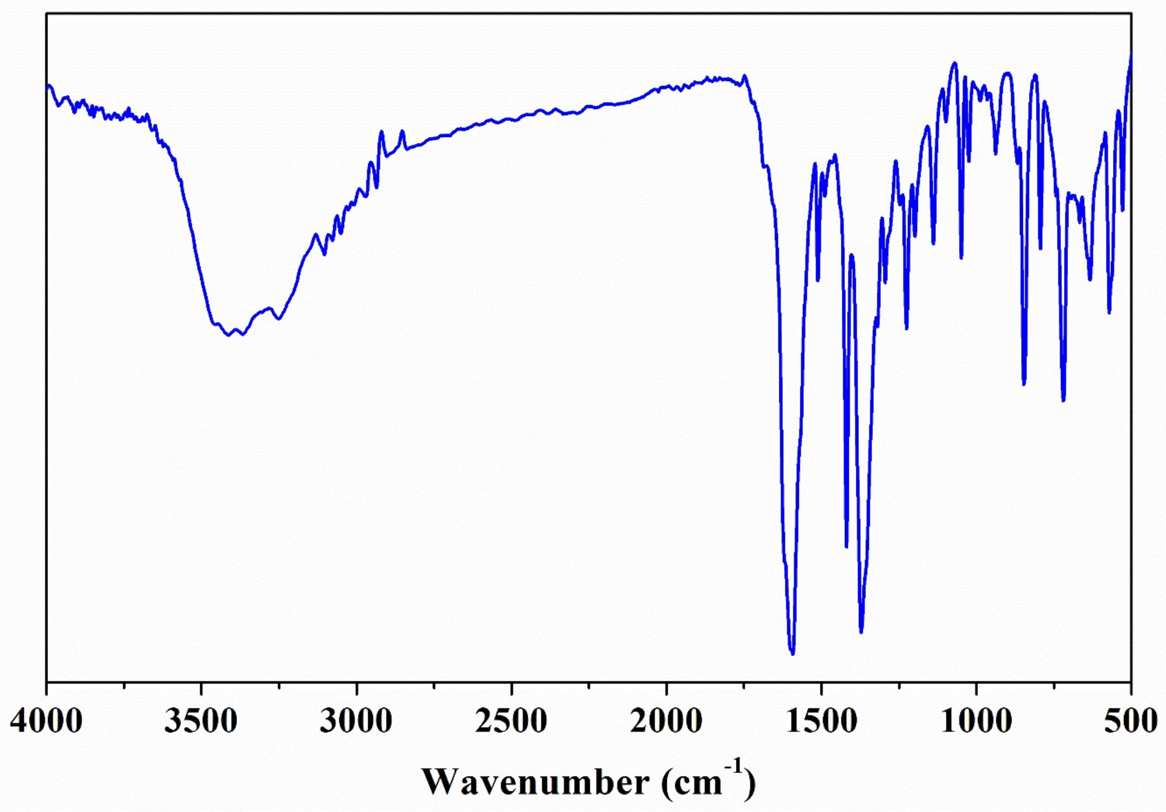

Fig. S1. IR Spectrum of **Zn-MOF-1** in the range 500-4000 cm^{-1}.

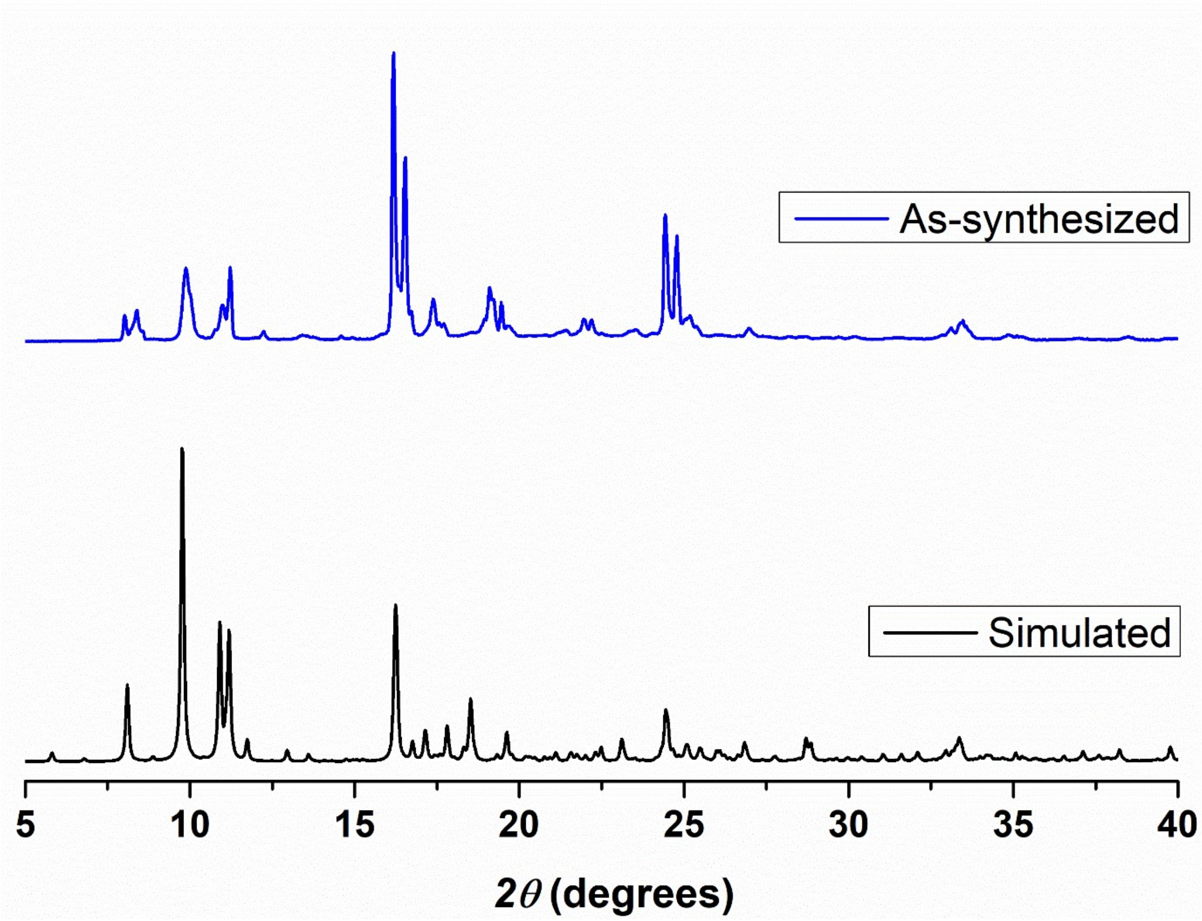

Fig. S2. Simulated (black color) powder X-ray diffraction pattern of **Zn-MOF-1** compared with the as-synthesized sample (blue color) of the MOF.

S2. Nanoindentation

Good quality single crystals of ***OP*** (***Open Phase***), ***IPs*** (***Intermediate Phases***) and ***CP*** (***Closed Phase***) were selected through an optical polarizing microscope for nanoindentation experiments. The crystals of ***IP-II, IP-II and CP*** were obtained by drying the ***OP*** crystals for 1 2, and 3 hours, respectively at RT. The crystals were initially washed with paraffin oil to remove any small crystals attached to the surface. Further, each crystal of ***OP***, ***IP***, and ***CP*** was firmly mounted on a metallic stud through a thin layer of cyanoacrylate glue. Nanoindentation experiments were performed using a three-sided pyramidal Berkovich diamond tip (radius ~100 nm) on the major face (001) of ***OP*** and ***IP***, and ***CP*** crystals, using the TI Premier Triboindenter from Hysitron, Minneapolis, USA, equipped with an *in-situ* AFM imaging capability. During nanoindentation, the loading and unloading rates were maintained at 0.4 mN/s with a hold time at the peak load (4 mN) of 30 s. Around five crystals of each ***OP, IPs*** and ***CP*** were examined and a minimum of 10 indentations were performed on each crystal to obtain consistent and reliable data. The AFM-scanned images containing the indentation impression was obtained to visualize the indent topology. The load *vs* depth of penetration (P-h) curves obtained were analyzed using the standard Oliver-Pharr (O-P) method to calculate elastic modulus (E) and hardness (H).[1,2] In case of significant pile-up of material against the indenter, the accurate values of H were calculated from the maximum indentation load, P_{max}, divided by the contact area, A, that was estimated from images of the indents.

S3. Face indexing

Face indexing of good quality single crystal of OP was performed at room temperature on a Rigaku Mercury 375R/M CCD (XtaLABmini) diffractometer with CrystalClear software, and the crystal faces were assigned (Fig. S3).

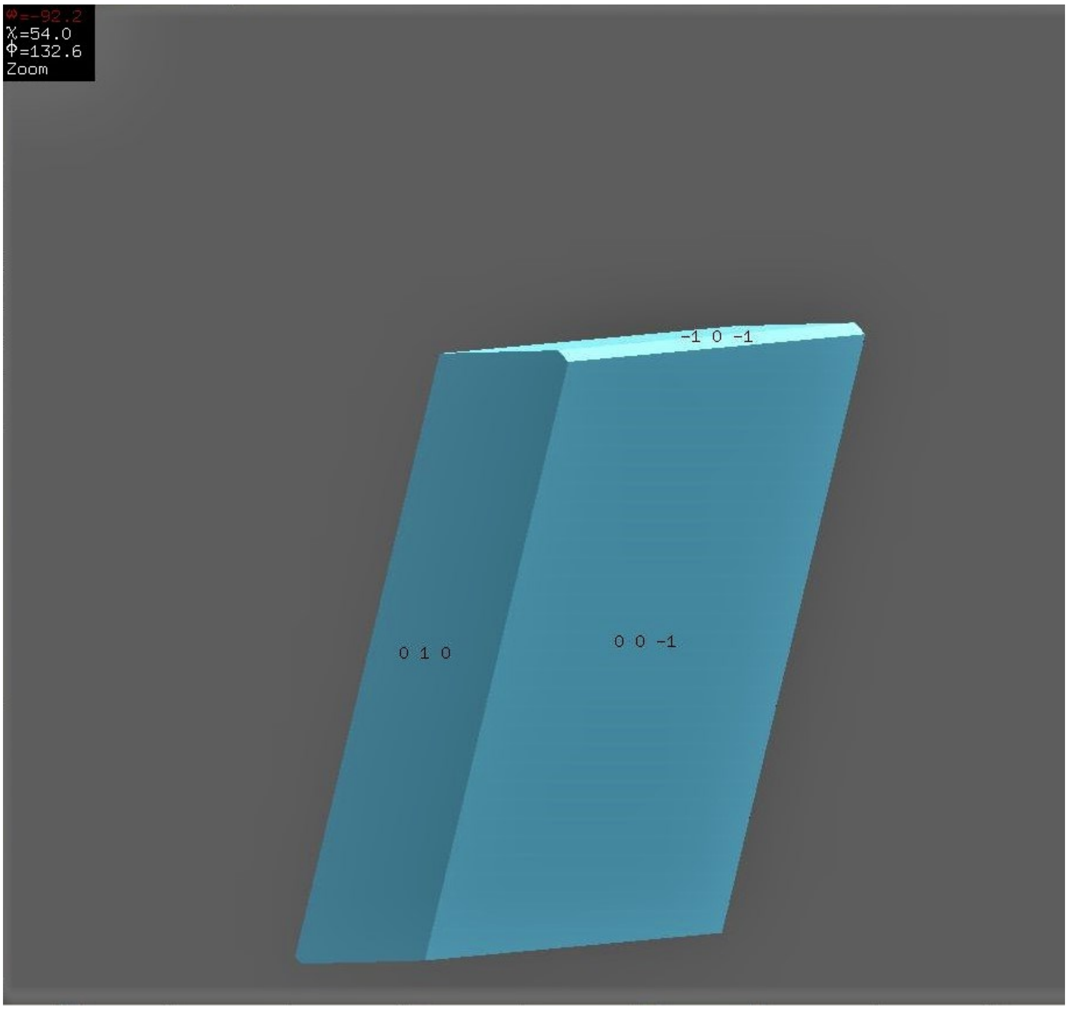

Fig S3. Face indexing image of ***OP*** phase. The major face is (**001)/(00-1).**

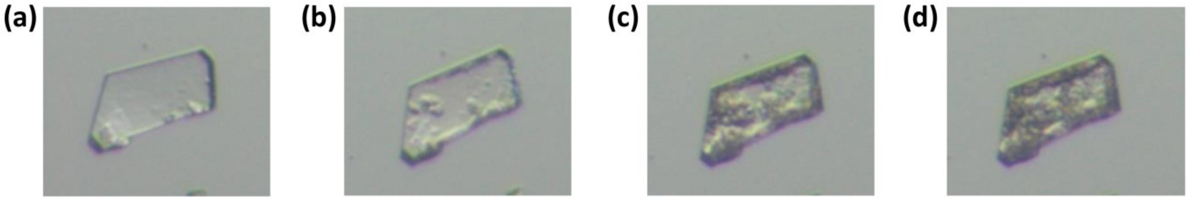

Fig S4. Microscopic images of the crystals of various phases of **Zn-MOF-1**. (a) At 0 minutes (***OP***); (b) At 1 hr (***IP-I***); (c) At 2 hrs (***IP-II***); (d) At 3 hrs (***CP***).

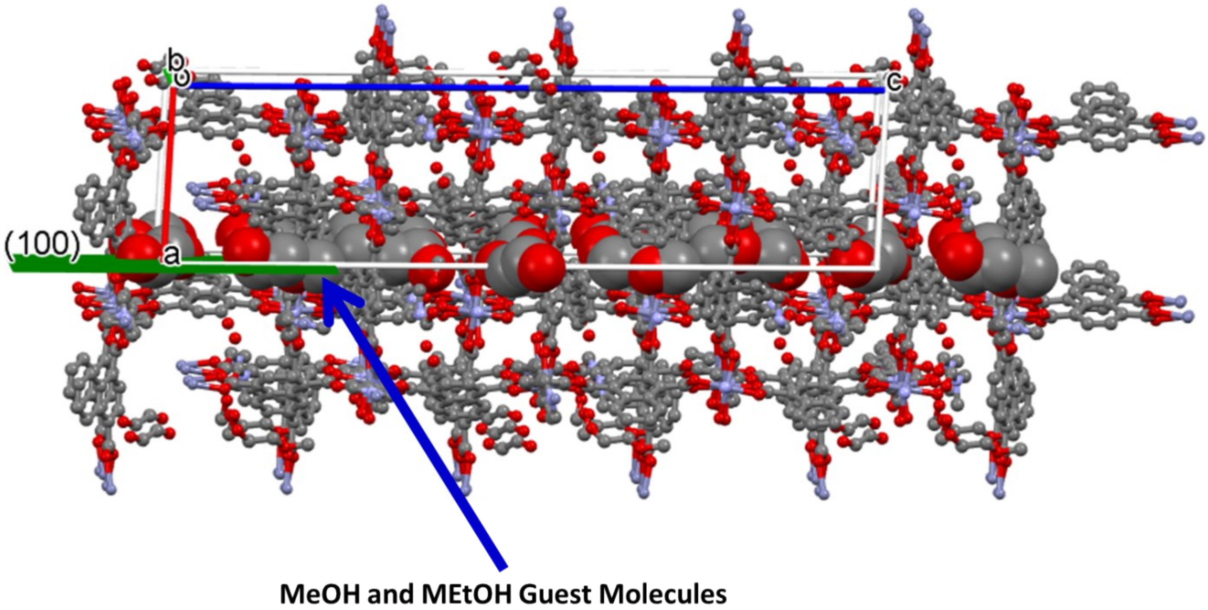

Fig. S5. Diagram showing the presence of MeOH and MEtOH guest molecules on (100) plane in the open phase of **Zn-MOF-1**.

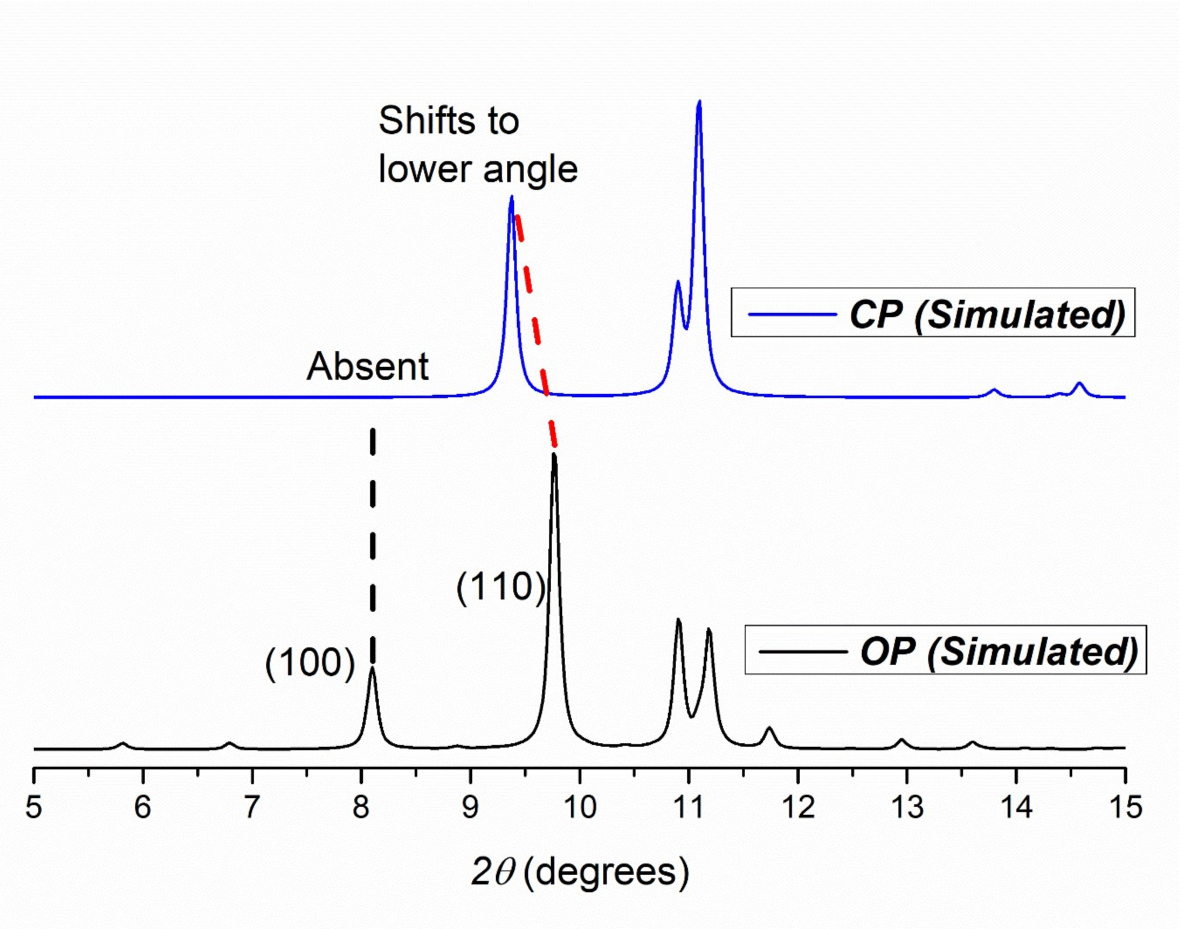

Fig. S6. Comparison of simulated PXRD patterns of ***OP*** and ***CP***s of **Zn-MOF-1** shows (100) peak is absent in the ***CP***. Also, (110) peak shifts to lower angle in the ***CP***.

References

1 W. C. Oliver, G. M. Pharr, *J. Mater. Res.*, 1992, **7**, 1564.

2 A. Bolshakov, G. M. Pharr, *J. Mater. Res.*, 1998, **13**, 1049.