# **Supporting Information**

# Synergistic role of microwave and perturbation towards synthesis of hierarchical porous MOFs with tunable porosity

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#### **Physical Measurements**

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover instrument using Cu-Ka radiation Bruker D8 (40 kV, 30 MA). Thermo gravimetric analysis (TGA) was carried out (Mettler Toledo) in N<sub>2</sub> atmosphere (flow rate = 50 ml min<sup>-1</sup>) in the temperature range 30 - 800 °C with 5 °C min<sup>-1</sup> heating rate. UV-Vis spectra of samples were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer. Infrared spectral studies were performed by making samples with KBr pellets using Bruker FTIR spectrometer in the region of 4000 - 400  $cm^{-1}$ . The scanning electron microscopy images were obtained by using a Nova Nanosem 600 FEI field emission scanning electron microscope (FESEM) with an accelerating voltage of 10 kV. Energy dispersive analysis of X-rays (EDX) was carried out using the field emission scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-3010 transmission electron microscope operating at 200 kV. The samples for FESEM and EDX were prepared by dispersing the sample in methanol then dropping the solution onto a piece of Silicon wafer. Similarly, for TEM, samples were prepared in previous method by drop casting methanolic dispersion onto a carbon-coated grid. Reactions under microwave stimuli were carried by transferring reaction mixture in 30 mL wide-neck vials by using MONOWAVE 200 (Anton Paar Monowave Series; Serial Number: 81919734; Instrument Software Version: 4.10.9376.7) microwave reactor. Adsorption measurement were carried out using AUTOSORB IQ2 and QUNATACHROME QUADRASORD-SI instrument for N<sub>2</sub> (77 K) and CO<sub>2</sub> (273 and 298 K). Approximately 100-150 mg samples were placed which had been prepared at 200 °C under a  $1 \times 10^{-1}$  Pa vacuum for about 12 h prior to each measurement of the isotherms. Ultrapure Helium gas at a certain pressure was allowed to diffuse into the sample cell for operating valve functions and dead volume measurement. The activated sample was placed into the sample cell (9 mm diameter), then the change of the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. However, all the operations were computer controlled and instinctive. Water vapor adsorptions were carried out at 298 K using BELSORP AQUA 3 solvent vapor analyzer. The sample preparation and measurement principle in solvent vapor adsorption were analogous to gas adsorption measurement.

# **Experimental Section**

#### Materials

All the reagents and solvents were commercially available and used as obtained from commercial supplies without any further purification. Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 2,5-dihydroxy-1,4-benzenedicarboxylic acid were obtained from Sigma Aldrich Chemical Co. N,N-dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), ethyl acetate, dimethylacetamide (DMA), acetone and tetrahydrofuran (THF) were obtained from Spectrochem Pvt. Ltd (Mumbai, India).

#### Synthesis of HNi-MOF-74/t

To prepare Ni-MOF-74/50, 0.198g of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.6811 mmol, 3.4 equiv) and 0.037g of 2,5-dihydroxy-1,4-benzenedicarboxylate (0.1968 mmol, 1 equiv) were dissolved in a 1:1:1 (v/v/v) combination of DMF (5.5 mL), ethanol (5.5 mL), water (5.5 mL) and stirred for 1 h. Then the reaction mixture is transferred to microwave reactor. The reaction mixture is heated to 100 °C in 20 min (a heating rate of 5 °C /min) and held at 100 °C for **40** minutes. The microwave power was controlled 850 W over the whole process with a constant 800 rpm stirring. Finally, it was collected in fresh DMF and washed subsequently with DMF and MeOH for 4 days.

A Similar method was followed to prepare all Ni-MOF-74-DMF/t where t (t stands for time in minute) varies from 20, 30, 50, 60, and 70 minutes in order to cognize the role of perturbation (or stirring) in microwave.

We performed an experiment similar to Ni-MOF-74-DMF/50 under microwave at 850 W with 0 rpm stirring (*i.e.*, without stirring) which revealed a typical type I isotherm of microporous MOF and the compound was mentioned as Ni-MOF-74/50W (5).

#### Synthesis of HNi-MOF-74 by varying solvent polarity

We choose a series of solvents with increasing polarity, different dimension and functional group starting from Ethyl acetate to DMSO. Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (3.4 equiv) and of 2,5-dihydroxy-1,4-benzenedicarboxylate (1 equiv) was dissolved in a 1:1:1 (v/v/v) combination of DMSO (5.5 mL), ethanol (5.5 mL), water (5.5 mL) and stirred for 1 h. Rest of the synthesis methods are identical to the previous one and named this material as HNi-MOF-74-DMSO/50 (10). Similarly, 5.5 mL of DMA, Acetone, THF and ethyl acetate are used to prepare HNi-MOF-74-DMA/50, HNi-MOF-74-Acetone/50, HNi-MOF-74-THF/50, and HNi-MOF-74-EA/50 under identical condition with 800 rpm stirring.

#### Solvothermal Synthesis of Ni-MOF-74

The synthetic procedure is similar to HNi-MOF-74 with respect to metal, ligand and solvent proportion. The homogeneous reaction mixture is transferred to 25 mL Teflon lined stainless-steel autoclaves. The autoclaves were kept at 100 °C for 24 h. After 24 h, the sample was removed from the oven and allowed to cool to room temperature. The resultant liquor was further washed by fresh DMF and MeOH. The MeOH exchange was performed for 4 days and final product was collected upon drying at 60 °C.

#### Characterization



Figure S1: FT-IR spectra of HNi-MOF-74-DMF/t.



Figure S2: PXRD patterns of HNi-MOF-74/60 and HNi-MOF-74/70.



Figure S3: TGA profile of HNi-MOF-74-DMF/20 (black), HNi-MOF-74-DMF/30 (brown), HNi-MOF-74-DMF/40 (green), HNi-MOF-74-DMF/50 (violet), Ni-MOF-74-DMF/50W (blue).



Figure S4: Comparative TGA profile of HNi-MOF-74-DMSO/50 and HNi-MOF-74-DMF/50.



**Figure S5:** TEM image of solvothermally prepared crystals (**Ni-MOF-74-SOL**) with distinguished nanocrystals (inset).



Figure S6: TEM image of Ni-MOF-74-DMF/50W (5) reveals the separated nanostructure generated through non-perturbed method.



Figure S7: TEM image of the bimodal microporous–mesoporous material HNi-MOF-74-DMSO/50 exhibited the fusion of nanoparticles.



Figure S8: FESEM (a) and EDX (b) study on HNi-MOF-74-DMSO/50.

# Analysis from Gas Adsorption Isotherm

# A detailed study for analyzing BET surface area, pore volume and pore size distribution and t-plot

The surface area, pore volume and pore size distribution were calculated from the  $N_2$  adsorption data of the corresponding samples using the ASiQwin software. The surface area was calculated using the Brunauer–Emmett–Teller (BET) theory, which is an extension from monolayer to multilayer adsorption. The BET equation is:

$$\frac{1}{\nu\left[\left(\frac{p_0}{P}\right)\right]} = \frac{C-1}{C\nu_m}(P/P_0) + \frac{1}{C\nu_m}$$

Where *P* and *P*<sub>0</sub> are the equilibrium and the saturation pressure of adsorbates at adsorption temperature, *v* is the adsorbed gas quantity, and  $v_m$  is the monolayer adsorbed gas quantity; *c* is the BET constant and can be expressed as:

$$c = \exp(\frac{E_1 - E_L}{RT})$$

 $E_1$  is the heat of adsorption for the first layer, and  $E_L$  is that for the second and higher layers.

The BET equation is an adsorption isotherm and can be plotted as a straight line with  $1/[v(P_0/P)-1]$  on the y-axis and  $P/P_0$  on the x-axis according to the experimental N<sub>2</sub> isotherms. The

value of the slope and the y-intercept of the straight line can be used to calculate the monolayer adsorbed gas quantity  $(v_m)$  and the BET constant. The total surface area  $S_{\text{total}}$  and the specific surface area  $S_{\text{BET}}$  are given by:

$$S_{\text{total}} = (v_{\text{m}} N \text{ s})/V$$

$$S_{\rm BET} = S_{\rm total}/a$$

Where *N* is Avogadro number, *S* is the adsorption cross section of the adsorbing species, *V* is the molar volume of the N<sub>2</sub> (adsorbed gas), and *a* is the mass of the solid adsorbent. We calculated the multi-point BET surface area of different samples using ASiQwin software in the  $P/P_0$  range approximately 0.05 to 0.30.

The total pore volume is calculated from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate. The pore volume and pore size distributions were calculated using the Density Functional Theory (DFT), which can provide sorption and phase behavior of fluids in narrow pores on a molecular level. Indeed, the Non-Local Density Functional Theory (NLDFT) and Grand Canonical Monte Carlo simulation (GCMC) methods can describe the local fluid structure near curved solid walls accurately; the adsorption isotherms in model pores are determined from intermolecular potentials of the liquid-liquid and solid-liquid interactions. The relation between isotherms derived from the above approaches and the experimental isotherm on a porous solid can be interpreted in terms of a Generalized Adsorption Isotherm (GAI) equation:

$$N\left(\frac{P}{P0}\right) = \int_{WMIN}^{WMAX} N\left(\frac{P}{P0}, W\right) f(W) dw$$

Where,  $N(P/P_0)$  = experimental adsorption isotherm data

W =pore width

 $N(P/P_0, W)$  = isotherm on a single pore of width W

f(W) = pore size distribution function

The assumption which is reflected from the GAI equation is that the total isotherm consists of a number of individual "single pore" isotherms multiplied by their relative distribution, f(W), over a range of pore sizes. The set of  $N(P/P_0, W)$  isotherms (kernel) for a given system can be obtained

by the DFT as indicated above. The pore size distribution can then be derived by solving the GAI equation numerically via a fast non-negative least square algorithm. We have used the ASiQwin software to calculate the pore size distribution using the NLDFT–N<sub>2</sub>-carbon equilibrium transition kernel at 77 K based on a slit-pore model.



**Figure S9:** N<sub>2</sub> Adsorption Isotherm for solvothermally prepared **Ni-MOF-74-SOL** with pore size distribution derived through NLDFT method (inset).



Figure S10: N<sub>2</sub> Adsorption Isotherm for HNi-MOF-74/60 and HNi-MOF-74/70 at 77 K.



**Figure S11:** NLDFT pore size distribution plot for **HNi-MOF-74/50** synthesized by different solvent medium.

## **Determining t-plot: Statistical thickness**

To determine micropore volume for a hierarchical system t-plot (volume *vs.* statistical thickness; *t*) is highly recommended. The *t* can be calculated independently by using the equation:

$$t(\text{\AA}) = \frac{10^4 V_{liq}}{S_{BET}}$$

Using this equation, a V vs. t plot is constructed from t vs.  $P/P_0$  data for a sample. The micropore surface areas can be calculated from the slopes and each successive interval calculation represents the area of all the micropores remaining unfilled. The calculations are continued until no further decrease in slope is found in the V *vs*. t plot, indicating that all the micropores have been filled.



**Figure S12**: The t-plot (calculated in the  $P/P_0$  range of 0.20 –0.50) method is a well-known technique which allows determining the micro- and/or mesoporous volumes (a) t-plot for nitrogen adsorbed at 77 K for all HNi-MOF-74/t and (b) HNi-MOF-74-Solvents.



Figure S13: CO<sub>2</sub> adsorption isotherm for HNi-MOF-74-DMF/50 at 273 K.



Figure S14:  $CO_2$  adsorption isotherm for HNi-MOF-74-DMSO/50 at 273 and 298 K, respectively.

### VB<sub>12</sub> encapsulation and corresponding kinetics study

We performed guest encapsulation study by immersing Vitamin  $B_{12}$ -MeOH (1.36×10<sup>-7</sup> M) solution of HNi-MOF-74-DMF/50. The solution is filtered and UV spectra are measured in different time interval to study the capture of VB<sub>12</sub> by MOF. To investigate the adsorption kinetics, we fitted the relative intensity change with time by utilizing mono-exponential function. The relative intensity *vs.* time (min) graph reveals the first order kinetics with  $5.11 \times 10^{-4}$  min<sup>-1</sup> rate constant value (Figure S15 (b)). We also performed the adsorption studies to find the VB<sub>12</sub> encapsulation in hierarchical MOF. The VB<sub>12</sub>@HNi-MOF-74-DMF/t was further dissolved in methanol. The solution became faint red due to desorption of VB<sub>12</sub> from mesopore of HNi-MOF-74-DMF/50 (Figure S16). The adsorption band of VB<sub>12</sub> at 549 nm is observed which clearly proves the structural integrity of VB<sub>12</sub> remain intact after encapsulation.



**Figure S15**: (a) Time dependent UV-Vis spectra of supernatant methanolic solutions of Vitamin  $B_{12}$  after introducing it with HNi-MOF-74-DMF/50 and (b) fitting of the relative intensity change with time by utilizing mono-exponential function.



Figure S16: UV-Vis spectra of methanolic solutions of  $VB_{12}$  encapsulated H-MOF and microporous MOF-74.