Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Synthesis and Engineering Porosity of mixed metal Fe_2Ni MIL-88B Metal-Organic Framework

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Preparation

In a typical synthesis, 0.67 mmol of $FeCl_3.6H_2O$ 99%, 0.33 mmol of corresponding $Ni(NO_3)_2.6H_2O$ 97% and 1 mmol of bdc 98% were dissolved in 10 ml of DMF. To this clear solution, 0.4 mmol of NaOH was added under stirring for 15 min. The mixture was then transferred into an Teflon-lined autoclave and heated at 100 ^oC for 15 h. Solid product was then recovered by filtration and washed several times with DMF.

Characterization

N_2 and CO_2 adsorption tests were carried out in an Autosorb 1 instrument, before analysis the samples were outgassed in vacuum for 3 hours at 150 ^oC. Specific surface area was calculated with the BET model in the linear range of P/Po = 0 – 0.15. KBr solid state FTIR was carried in a FT-BIORAD 450s system. MgO solid state UV-VIS was carried in a Cary 300 instrument. Powder X-ray diffraction (XRD) patterns were collected on a Bruker SMART APEX II X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 4 – 20° at a scan rate of 1.0° min^{-1}. For XRD measurement of samples in Figure 3 and for crystal lattice calculation, the samples were dried in vacuum overnight at 100 ^oC, then the analysis was taken immediately. Peak fitting was carried out using Jade software package (http://www.materialsdata.com/).

Simulation of Fe_3-MIL-88B XRD pattern was done on the crystalography data reported by Férey et al [1] using Mercury software package (https://www.ccdc.cam.ac.uk/products/mercury/)

Scanning electron microscopy (SEM) images were taken on a JEOL 6360 instrument at accelerating voltage of 3 kV

FTIR

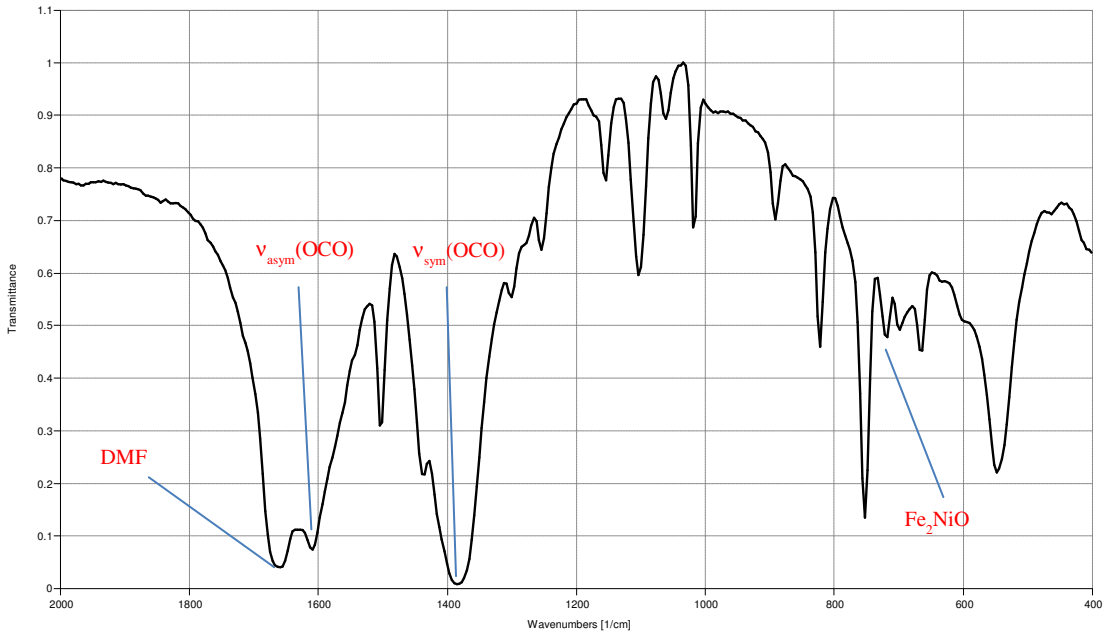

Figure S1. FTIR spectra of Fe_2Ni-MIL-88B.DMF

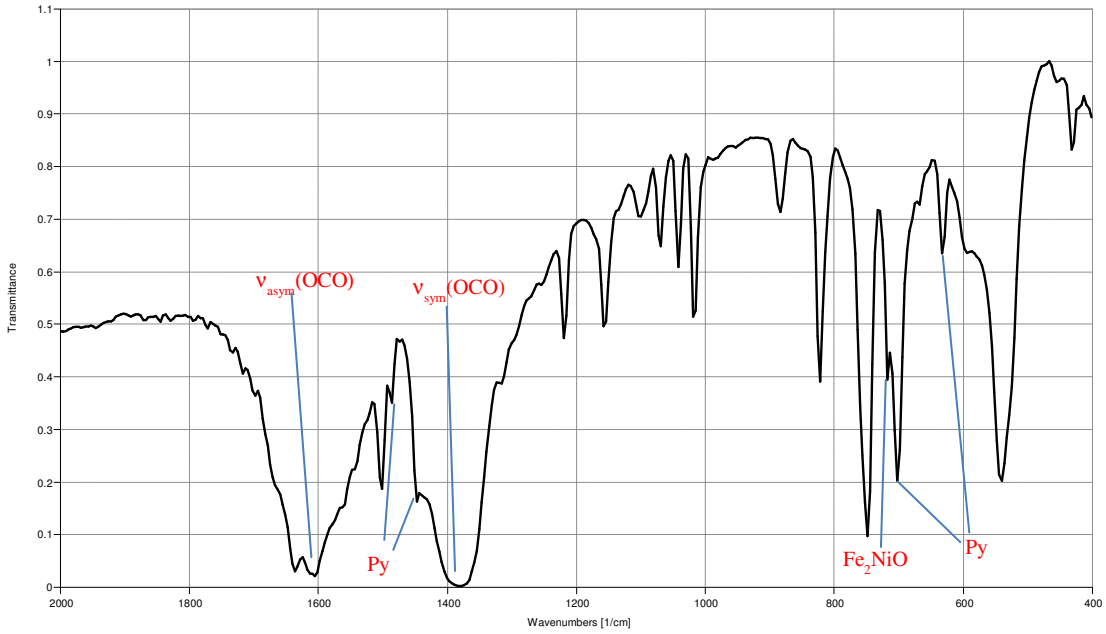

Figure S2. FTIR spectra of Fe_2Ni-MIL-88B.Py

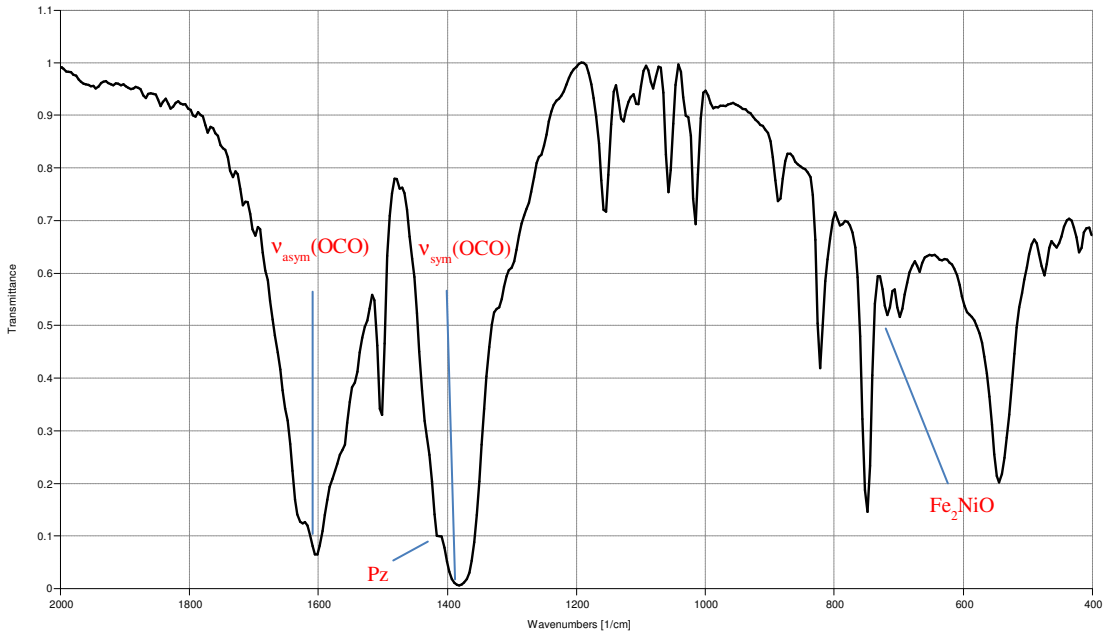

Figure S3. FTIR spectra of Fe_2Ni-MIL-88B.Pz

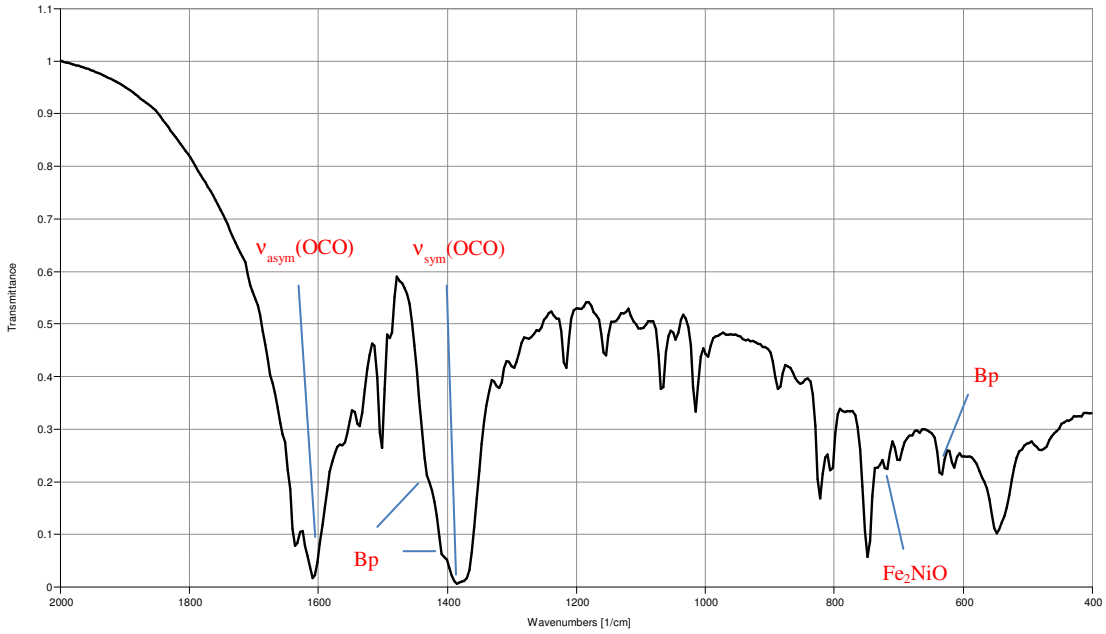

Figure S4. FTIR spectra of Fe_2Ni-MIL-88B.Bp

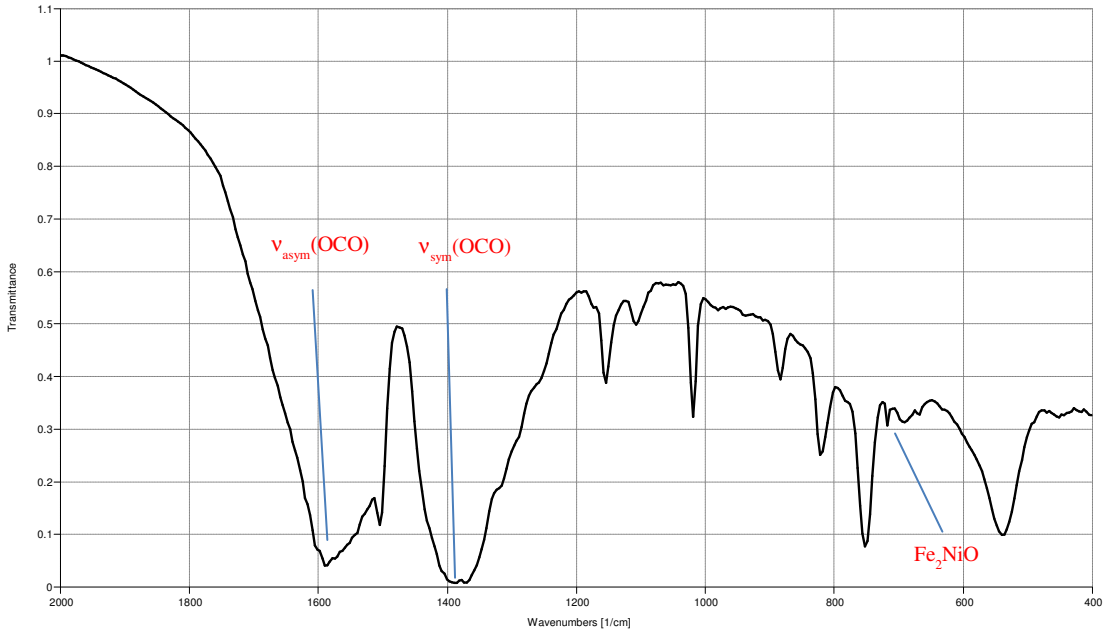

Figure S5. FTIR spectra of Fe_2Ni-MIL-88B.H_2O

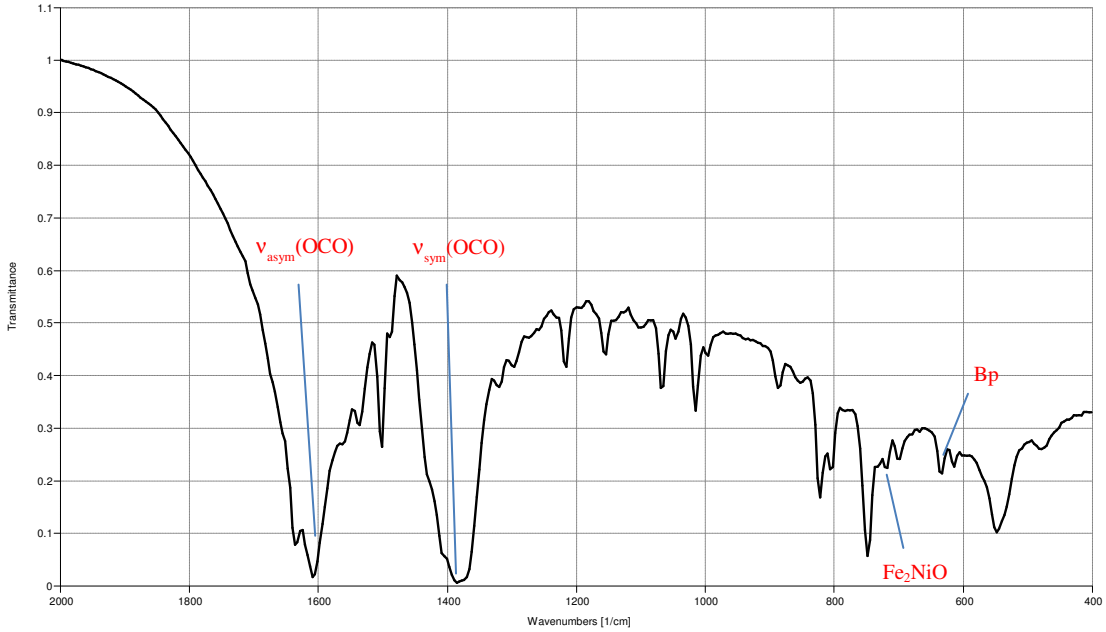

Figure S6. FTIR spectra of Fe_3-MIL-88B.DMF

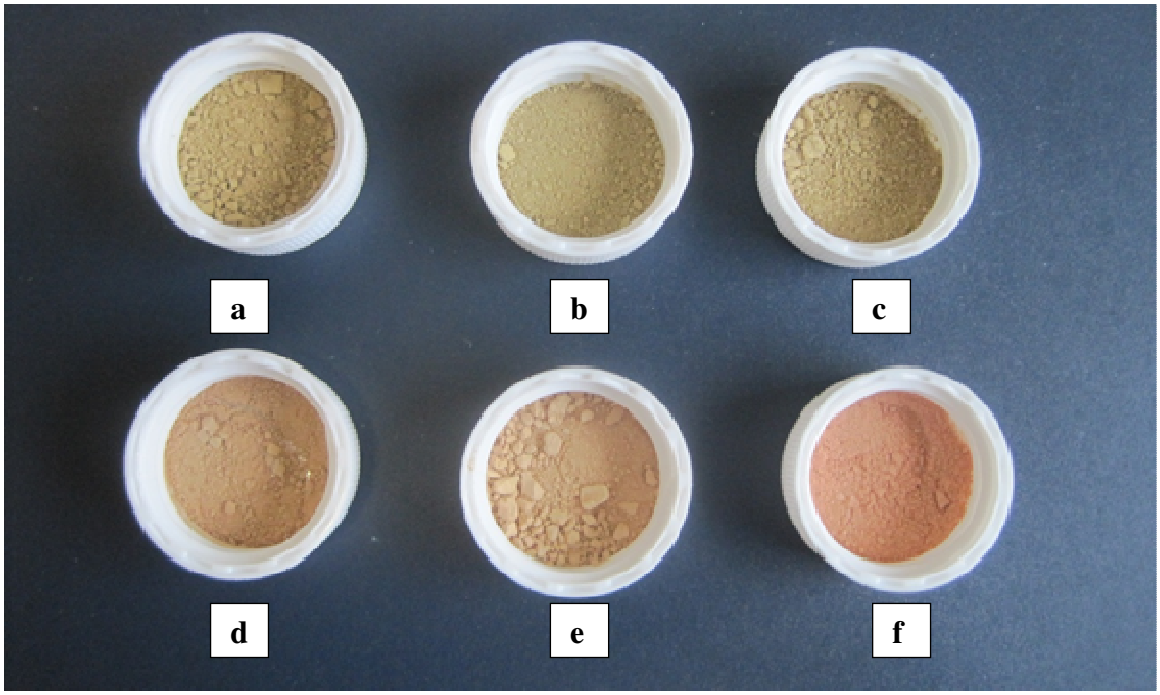

Figure S7. Images of Fe_2Ni-MIL-88B.Bp (a), Fe_2Ni-MIL-88B.Pz (b), Fe_2Ni-MIL-88B.Py (c), Fe_2Ni-MIL-88B.DMF (d) Fe_2Ni-MIL-88B.H_2O (e) and Fe-MIL-88B.DMF (f).

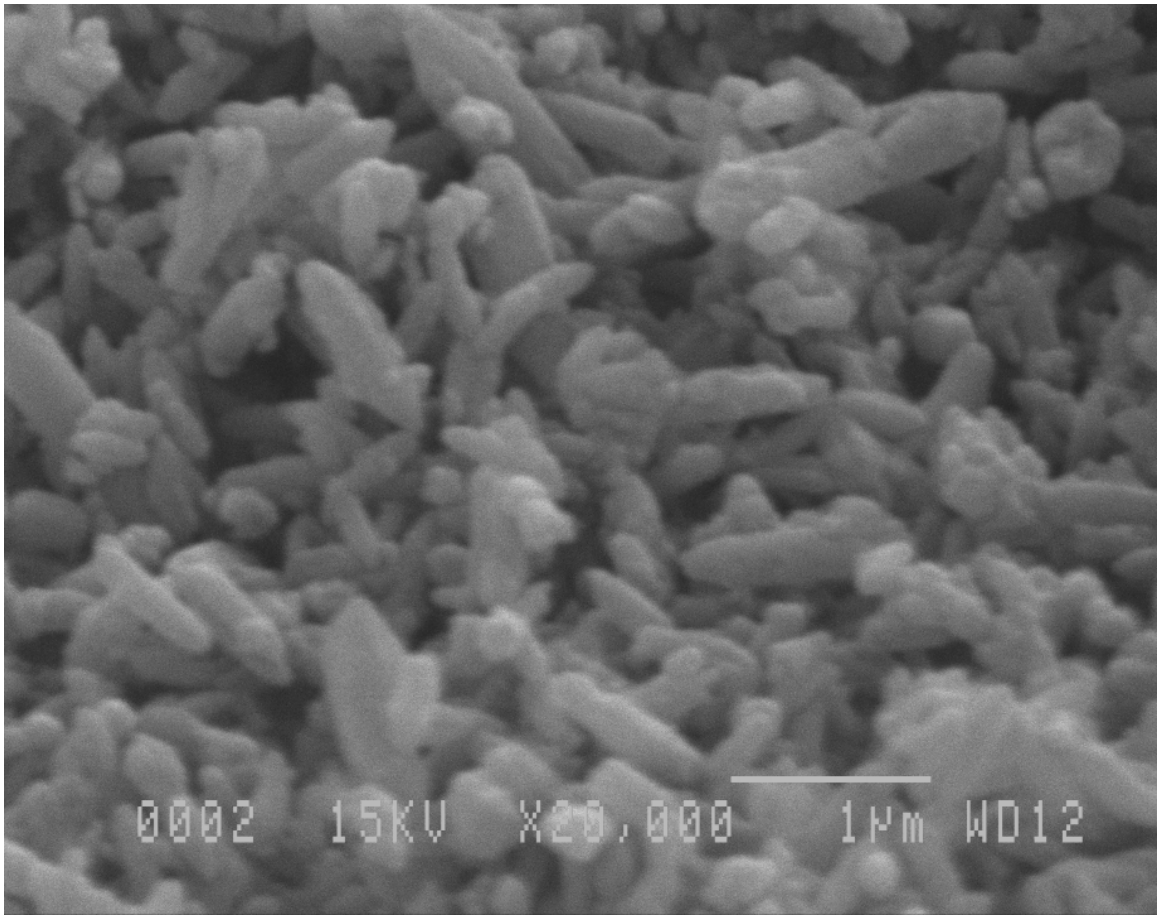

Figure S8. SEM image of as-synthesized Fe_2Ni-MIL-88B.DMF

Ligand exchange reactions:

+ DMF => H_2O: 0.25 g of Fe_2Ni-MIL-88B.DMF was added with 10 ml of water. The obtained mixture was stirred at room temperature for 3 hours, and then the solid was recovered by filtration and dried at 100 ^{0}C overnight. XRD pattern showed in Figure 3e

+ H_2O=>DMF: 0.25 g of Fe_2Ni-MIL-88B.H_2O was added with 10 ml of DMF. After stirring for 30 min, the mixture was transferred into an autoclave and it was placed in oven at 110 ^{0}C for 3 days. The product was recovered by filtration and washed several times with DMF (Figure S9), BET specific surface area: 320 m^2/g.

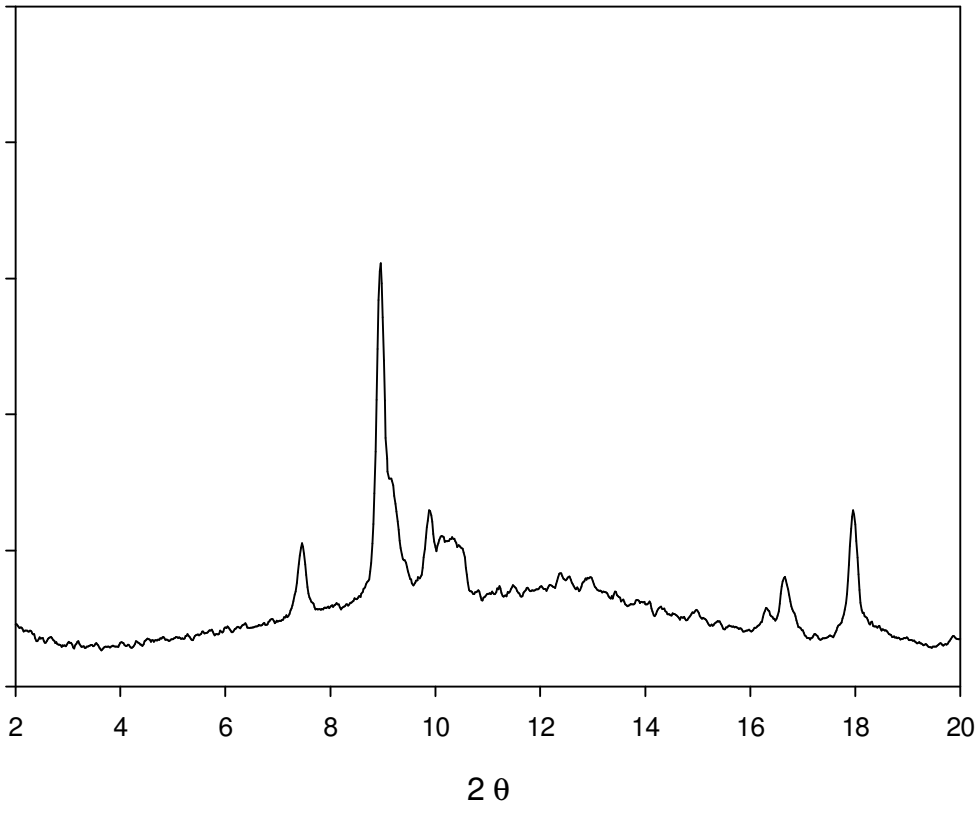

Figure S9: XRD pattern of Fe_2Ni-MIL-88B.DMF obtained from Fe_2Ni-MIL-88B.H_2O

+ DMF=>Py: 0.25 g of Fe_2Ni-MIL-88B.DMF was added with 10 g of pyridine. Very quickly the solid changed its color from brown to olive green. The mixture was stirred for 3 hours. The product was filtrated and dried in vacuum at 100 ^oC overnight. XRD pattern showed in Figure 3c.

+ Py = > DMF. 0.25 g of Fe_2Ni-MIL-88B.Py was added with 10 ml of DMF. The mixture was stirred at 100 ^oC for 3 days while the color gradually changed from olive green to yellow. The product was filtrated, washed with DMF and dried in vacuum at 100 ^oC overnight (Figure S10). BET specific surface area: 340 m^2/g.

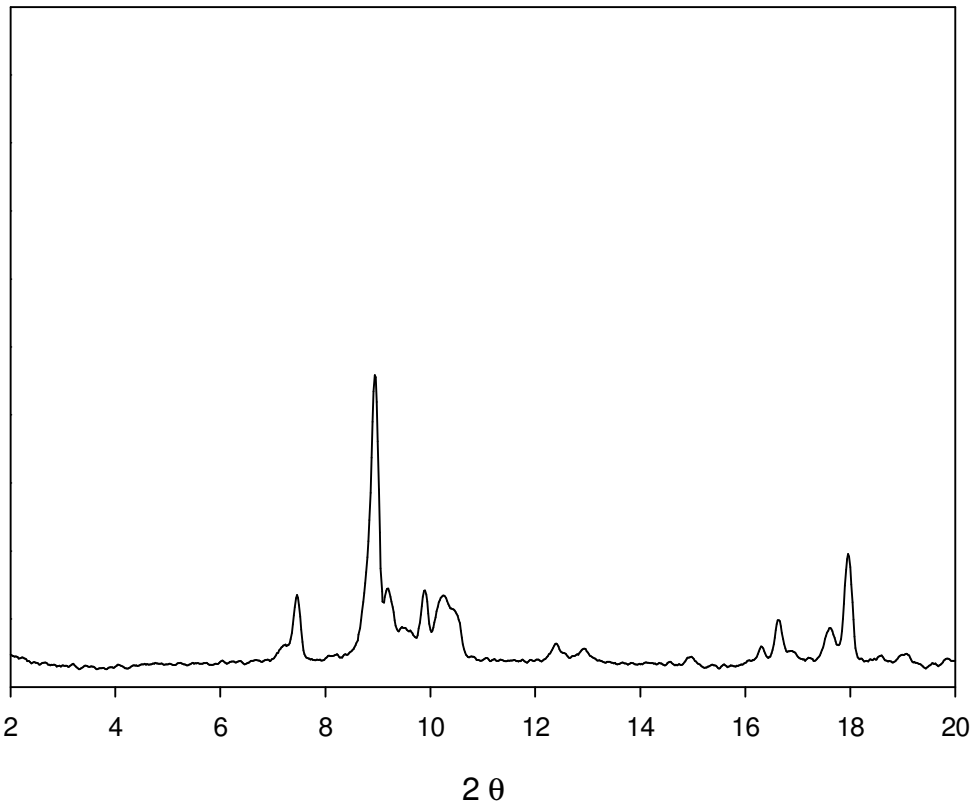

Figure S10: XRD pattern of Fe_2Ni-MIL-88B.DMF obtained from Fe_2Ni-MIL-88B. Py

+ DMF = > Pz: 0.25 g of Fe_2Ni-MIL-88B.DMF was added with 10 g of pyrazine. The mixture was heated to 70 ^oC as pyrazine melted, stirring was applied for 3 hours. The olive green product was recovered by hot filtration and dried in vacuum at 100 ^oC overnight. XRD pattern showed in Figure 3b.

+ Pz => DMF: 0.25 g Fe_2Ni-MIL-88B.Pz was added with 10 ml of DMF, the mixture was transferred into an autoclave and heated at 100 ^oC for 3 days. Brown solid product was filtrated and washed with DMF before drying in vacuum at 100 ^oC overnight (Figure S11). BET specific surface area: 325 m^2/g.

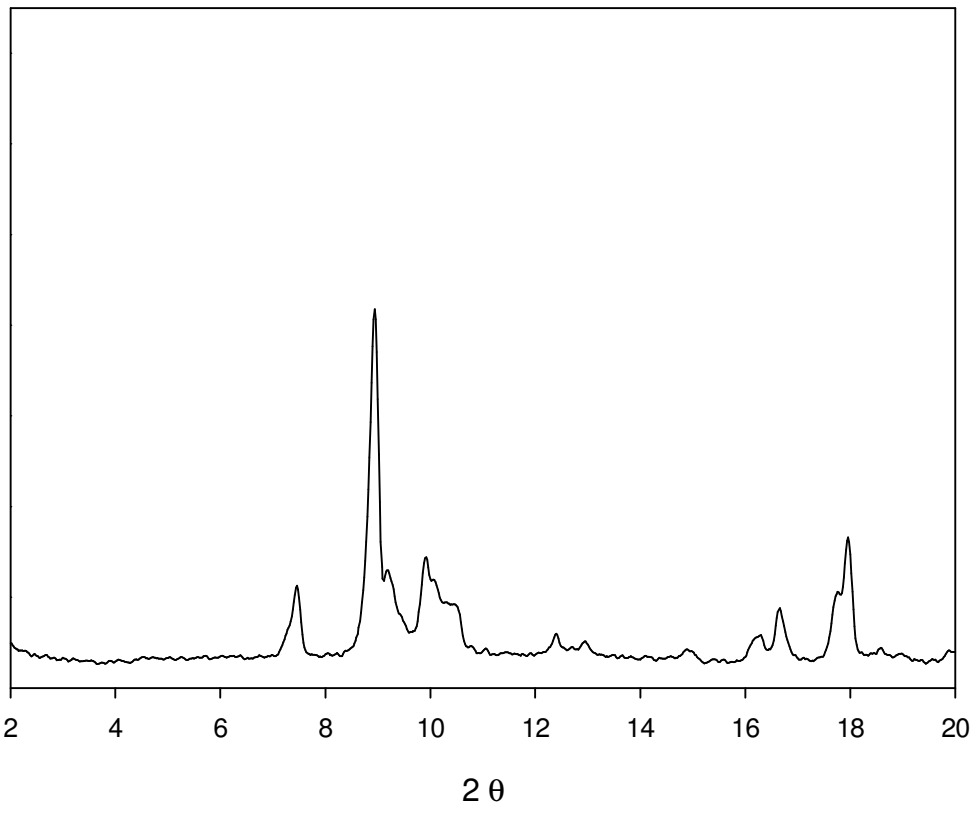

Figure S11: XRD pattern of Fe_2Ni-MIL-88B.DMF obtained from Fe_2Ni-MIL-88B. Pz

+ Pz = > H_2O: 0.25 of Fe_2Ni-MIL-88B.Pz in a vial was added with 15 ml of water. The vial was then sealed and stirred at 95 ^oC. After 3 hours the brown product was filtrated and dried in vacuum at 100 ^oC overnight (Figure S12). BET specific surface area: 15 m^2/g.

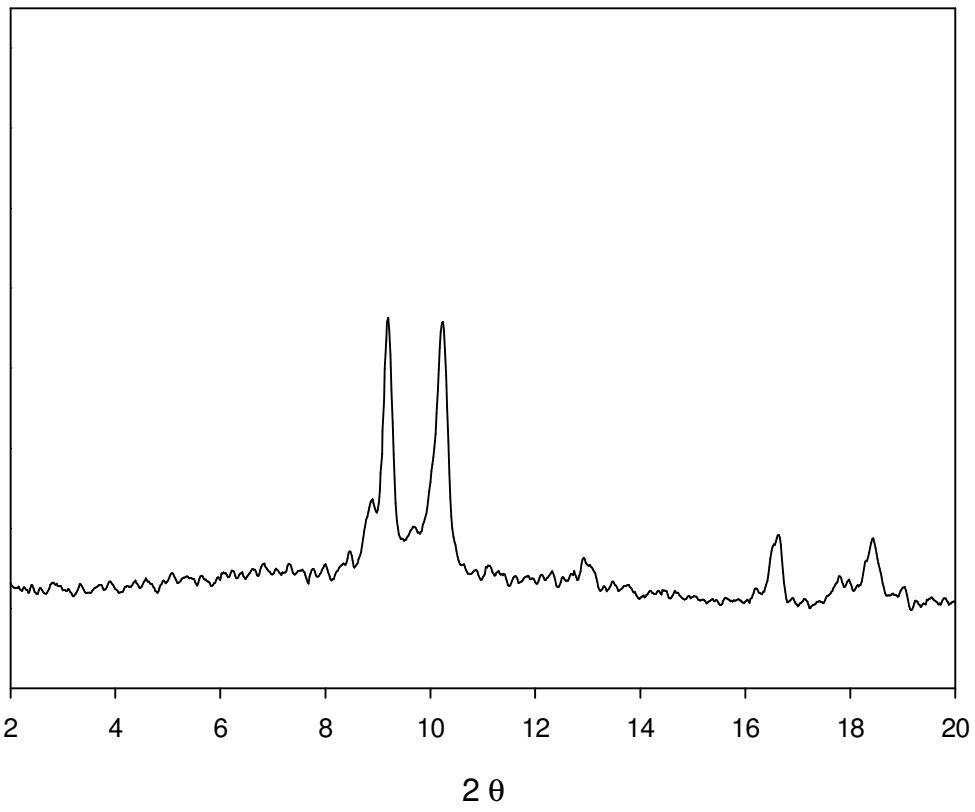

Figure S12: XRD pattern of Fe_2Ni-MIL-88B.H_2O obtained from Fe_2Ni-MIL-88B. Pz

+ H_2O => Pz: 0.25 g of Fe_2Ni-MIL-88B.H_2O was added with 10 g of pyrazine. The mixture was heated at 100 ^oC for 3 days. The olive green product was recovered by filtration and dried in vacuum at 100 ^oC overnight (Figure S13). BET specific surface area: 420 m^2/g.

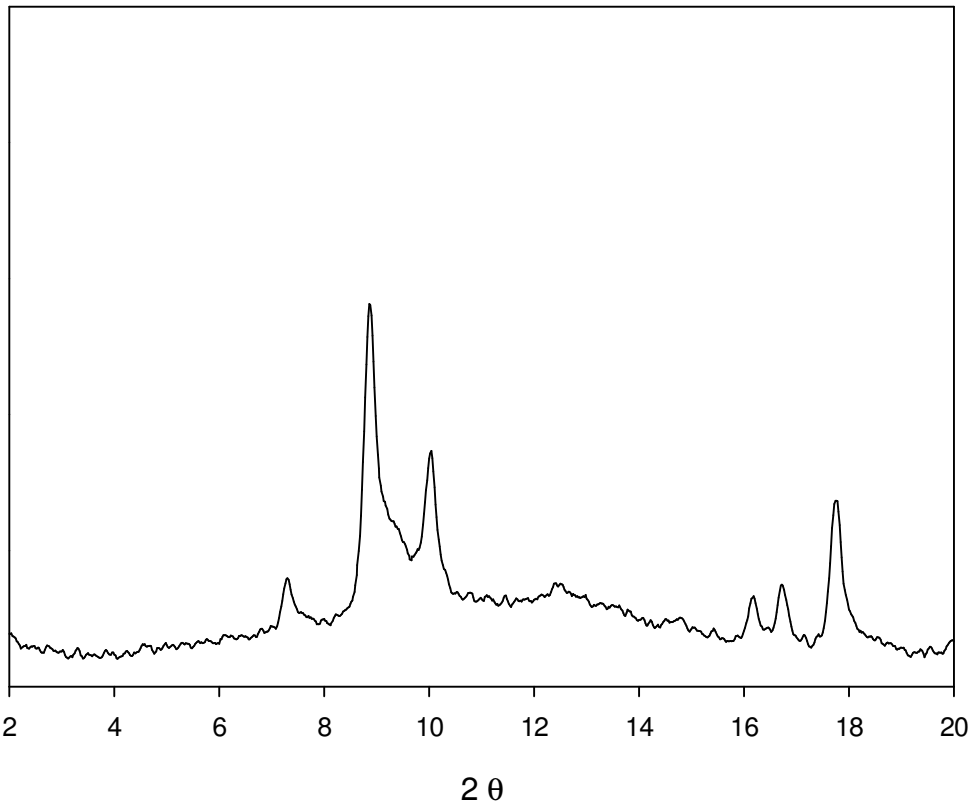

Figure S13: XRD pattern of Fe_2Ni-MIL-88B.Pz obtained from Fe_2Ni-MIL-88B. H_2O

+ Py => H_2O: 0.25 of Fe_2Ni-MIL-88B.Py in a vial was added with 15 ml of water. The vial was then sealed and stirred at 95 ^oC. After 3 hours the brown product was filtrated and dried in vacuum at 100 ^oC overnight (Figure S14), BET specific surface area: 10 m^2/g.

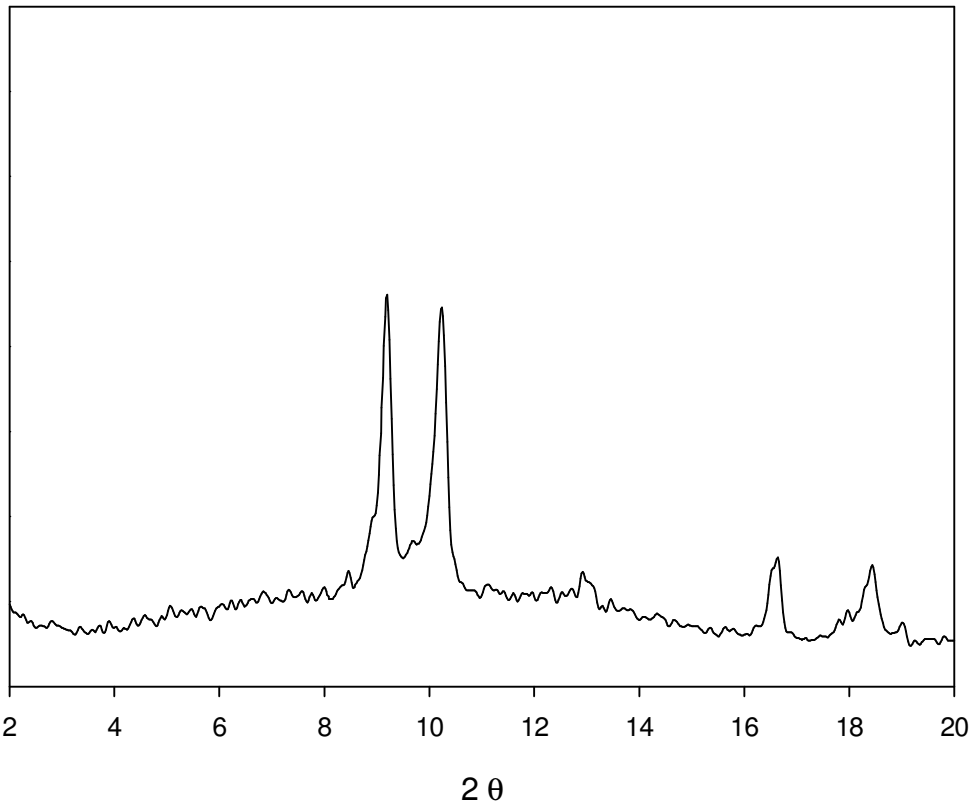

Figure S14: XRD pattern of Fe_2Ni-MIL-88B.H_2O obtained from Fe_2Ni-MIL-88B. Py

+ H_2O => Py: 0.25 g of Fe_2Ni-MIL-88B.H_2O was added with 10 ml of pyridine. The mixture was sealed in a vial and stirred at 100 ^oC for 4 days. Olive green product was filtered and dried in vacuum at 100 ^oC overnight (Figure S14). BET specific surface area: 530 m^2/g

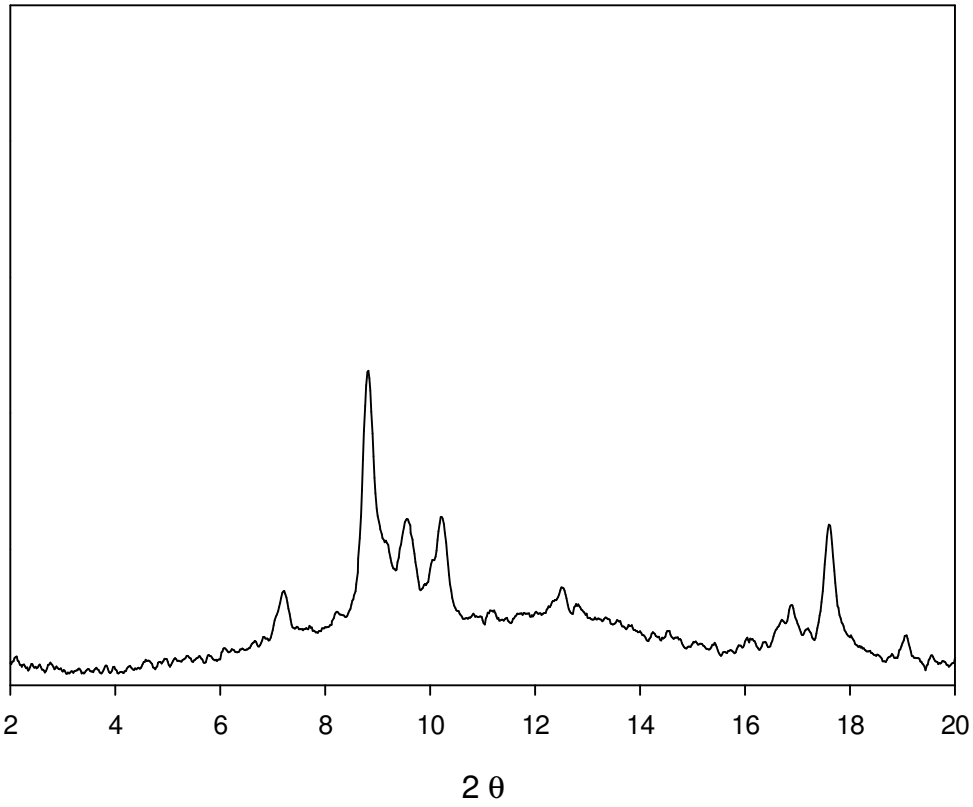

Figure S15: XRD pattern of Fe_2Ni-MIL-88B.Py obtained from Fe_2Ni-MIL-88B. H_2O

+ DMF => Bp: 0.16 g of bipyridine was introduced to 2 ml of DMF, to this solution 0.12 g of Fe_2Ni-MIL-88B.DMF was added. The mixture was then stirred at 100 ^oC for 4 days. Olive green product was filtered and dried in vacuum at 100 ^oC. XRD pattern showed in Figure 3a

+ Bp => DMF: 0.12 g of Fe_2Ni-MIL-88B.Bp was added with 15 ml of DMF, the mixture as transferred into an autoclave and it was placed in an oven at 100 ^oC for 6 days. Brown product

was filtered and washed with DMF before drying in vacuum overnight at 100 °C (Figure S16). BET specific surface area: 330 m^2/g.

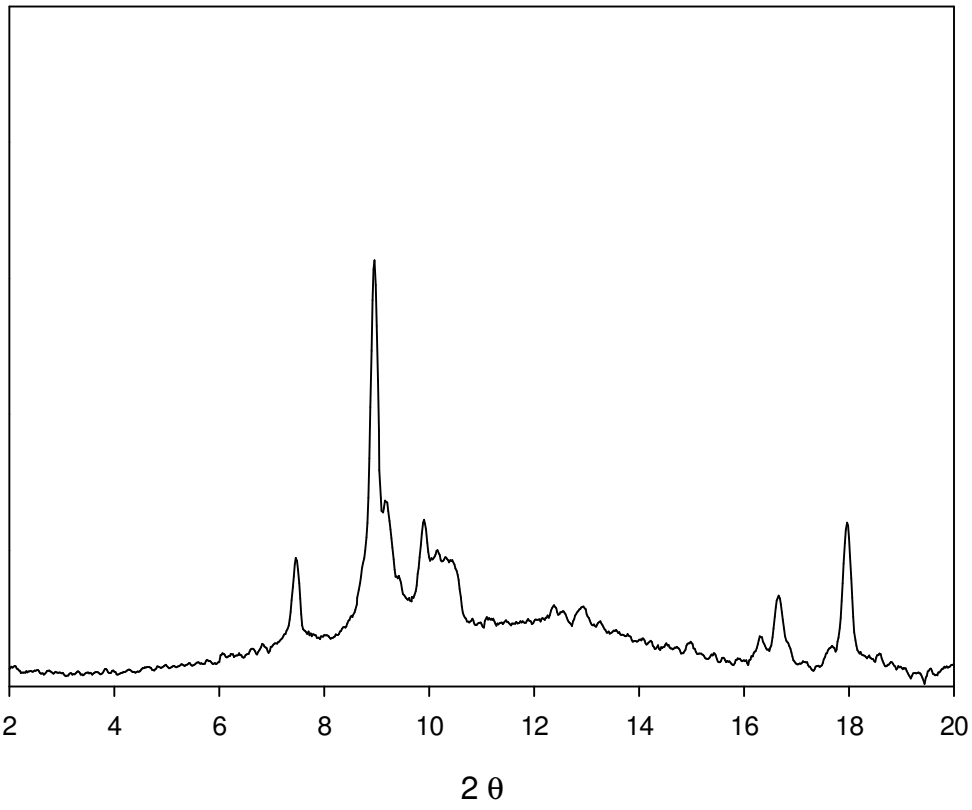

Figure S16: XRD pattern of Fe_2Ni-MIL-88B.DMF obtained from Fe_2Ni-MIL-88B.Bp

References

(1) S. Bauer, C. Serre, T. Devic, P. Horcajada, J. r. m. Marrot, G. r. Férey, N. Stock, *Inorg. Chem.* **2008**, *47*, 7568