

# Supplementary Information

## **Adjusting the Stability of Metal-Organic Frameworks under Humid Conditions by Ligand Functionalization**

Himanshu Jasuja, Yougui Huang and K. S. Walton\*

*School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta Georgia 30332 USA,*

\* Corresponding author. E-mail: [krista.walton@chbe.gatech.edu](mailto:krista.walton@chbe.gatech.edu) Fax: 1-404-894-2866

## Supplementary Index

1. Synthesis procedure for MOFs.....	S2
1.1 Preparation of Zn-1,4-NDC-DABCO or DMOF-N.....	S2
1.2 Preparation of Zn-ADC-DABCO or DMOF-A.....	S2
1.3 Preparation of Zn-BDC-TMBDC-DABCO or DMOF-TM1.....	S2
1.4 Preparation of Zn-TMBDC-DABCO or DMOF-TM2.....	S3
1.5 Preparation of Zn-BDC-NO <sub>2</sub> -DABCO or DMOF- NO <sub>2</sub> .....	S3
1.6 Preparation of Zn-BDC- Br-DABCO or DMOF-Br.....	S3
1.7 Preparation of Zn-BDC-Cl <sub>2</sub> -DABCO or DMOF- Cl <sub>2</sub> .....	S3
1.8 Preparation of Zn-BDC-OH-DABCO or DMOF-OH.....	S4
2. Characterization.....	S4
2.1 PXRD (Powder X-Ray Diffraction).....	S4
2.2 Surface Area Analysis.....	S12
2.3 Water Vapor Adsorption Isotherms Measurements.....	S17

## **1. Synthesis procedure for MOFs**

### **1.1. Preparation of Zn-1,4-NDC-DABCO**

Synthesis of Zn-1,4-NDC-DABCO was done as per the literature procedure<sup>[1]</sup> i.e. by mixing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.6 mmol), NDC (0.6 mmol) and DABCO (0.3 mmol) in DMF (9 mL) at room temperature in a glass beaker and the resulting slurry was stirred for 3 hrs. After filtering the white precipitate, the resulting solution was poured into a glass vial which was placed in a sand bath and finally sand bath was kept in a preheated oven at 120 °C for 48 hrs. After the solution was cooled to room temperature in air, the resulting solid was filtered and repeatedly washed with DMF. The resulting brick-shaped colorless crystals obtained after drying were transferred to a vial. Activated samples for gas adsorption measurements were prepared by heating the as-synthesized compound at 110° overnight in the degasser.

### **1.2. Preparation of Zn-ADC-DABCO**

Zn-ADC-DABCO was synthesized according to literature procedure<sup>[2]</sup> i.e.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol), ADC (1 mmol), were dissolved in DMF (5 mL) at room temperature in a glass beaker. After DABCO (0.5 mmol) and MeOH (5 mL) were added to the mixture, resulting slurry was stirred for 12-18 hrs. After filtering the white precipitate, the filtrate was poured into a Teflon autoclave, which was kept in a preheated oven at 120 °C for 48 hrs. After the solution was left to cool to room temperature in air, the resulting solid was filtered and repeatedly washed with DMF. The yellowish brick-shaped crystals obtained after drying were transferred to a vial. Crystals of Zn-ADC-DABCO were activated by heating the as-synthesized compound at 110°C overnight in the degasser.

### **1.3. Preparation of Zn-BDC-TMBDC-DABCO**

Synthesis of Zn-BDC-TMBDC-DABCO was performed following literature procedure<sup>[1]</sup> i.e.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.6 mmol), BDC (0.3 mmol), TMBDC (0.3 mmol) and DABCO (0.3 mmol) were mixed in DMF (9 mL) at room temperature in a glass beaker and resulting slurry was stirred for 3 hrs. The white precipitate was filtered and the resulting solution was poured into a glass vial which was placed in a sand bath and finally sand bath was kept in a preheated oven at 120 °C for 48 hrs. Solution was cooled to room temperature in air followed by filtering the resulting solid which was repeatedly washed with DMF. The resulting colorless brick-shaped crystals obtained after drying was transferred to a vial. Activated samples for gas adsorption measurements were prepared by heating the as-synthesized compound at 110° overnight in the degasser.

#### **1.4. Preparation of Zn-TMBDC-DABCO**

Zn-TMBDC-DABCO was prepared in a similar manner as described by Dybsteven et. al.<sup>[1]</sup> Therefore, Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.63 mmol), TMBDC (0.63 mmol) and DABCO (0.31 mmol) were mixed in 15ml of DMF in a glass beaker at room temperature and then the mixture was homogenized by stirring for 2-3 hrs. The resulting solution was transferred to teflon-lined stainless steel bomb reactor, kept in a preheated oven at 120 °C for 48 hrs. In the end, solution was allowed to cool to room temperature in air and then the resulting white colored solid was filtered and repeatedly washed with DMF. Crystals of Zn-TMBDC-DABCO were activated by heating the as-synthesized compound at 110°C overnight in the degasser.

#### **1.5. Preparation of Zn-BDC-NO<sub>2</sub>-DABCO**

The yellow crystals of Zn-BDC-NO<sub>2</sub>-DABCO were synthesized in a similar fashion as reported by Uemura et. al.<sup>[3]</sup> i.e. by mixing Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (2 mmol), BDC-NO<sub>2</sub> (2 mmol) and DABCO (1 mmol) in DMF (30 mL) at room temperature and resulting slurry was stirred for 5-10 minutes . The solution was transferred into a Teflon autoclave and then it was kept in a preheated oven at 120 °C for 48 hrs. After the reaction, the product was filtered and repeatedly washed with DMF. Activated samples for gas adsorption measurements were prepared by heating the as-synthesized compound at 110° overnight in the degasser.

#### **1.6. Preparation of Zn-BDC-Br-DABCO**

Synthesis of Zn-BDC-Br-DABCO was performed following literature procedure<sup>[4]</sup> i.e. Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (2 mmol), BDC-Br (2 mmol) and DABCO (1 mmol) were mixed in 30 ml of DMF at room temperature in a glass beaker and resulting slurry was stirred for 5-10 minutes. Subsequently, solution was poured into a Teflon autoclave, which was kept in a preheated oven at 120 °C for 48 hrs. Solution was cooled to room temperature in air and then the resulting solid was filtered and repeatedly washed with DMF. The resulting brick-shaped colorless crystals obtained after drying, were transferred to a vial. Crystals of Zn-BDC-Br-DABCO were activated by heating the as-synthesized compound at 110°C overnight in the degasser.

#### **1.7. Preparation of Zn-BDC-Cl<sub>2</sub>-DABCO**

The crystals of Zn-BDC-Cl<sub>2</sub>-DABCO were synthesized in a similar fashion as reported by Uemura et. al.<sup>[4]</sup> i.e. by mixing Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (2 mmol), BDC-Cl<sub>2</sub> (2 mmol) and DABCO (1 mmol) in 30 ml of DMF in a glass beaker at room temperature and subsequently, homogenized by stirring for 5-10 minutes. The resulting solution was

transferred to teflon-lined stainless still bomb reactor, kept in a preheated oven at 120 °C for 48 hrs. In the end, solution was allowed to cool to room temperature in air and then the resulting white colored solid was filtered and repeatedly washed with DMF. Activated samples for gas adsorption measurements were prepared by heating the as-synthesized compound at 110°C overnight in the degasser.

### **1.8. Preparation of Zn-BDC-OH-DABCO**

The colorless crystals of Zn-BDC-OH-DABCO were synthesized according to literature procedure<sup>[5]</sup> i.e. by mixing Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol), BDC-OH (1 mmol) and DABCO (0.5 mmol) in 10ml DMF at room temperature and resulting slurry was stirred for 5-10 minutes . The solution was transferred into a Teflon autoclave and then it was kept in a preheated oven at 110 °C for 24 hrs. After the reaction, the product was filtered and repeatedly washed with DMF. Crystals of Zn-BDC-OH-DABCO were activated by heating the as-synthesized compound at 110°C overnight in the degasser.

## **2. Characterization**

### **2.1 PXRD (Powder X-Ray Diffraction)**

Powder X-ray diffraction patterns (PXRD) were collected using an X'Pert X-ray PANalytical diffractometer with an X'accelerator module using Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at room temperature, with a step size of 0.02° in two theta (2 $\theta$ ). From these patterns, the phase purity of as-synthesized samples can be confirmed by comparison with the simulated patterns from single crystal X-ray diffraction (Figs. S1-S8). PXRD patterns of as-synthesized samples were also compared with patterns of water-exposed samples and with samples obtained after activating/ regenerating the water-exposed samples to determine the stability of MOFs under humid conditions (see main text).

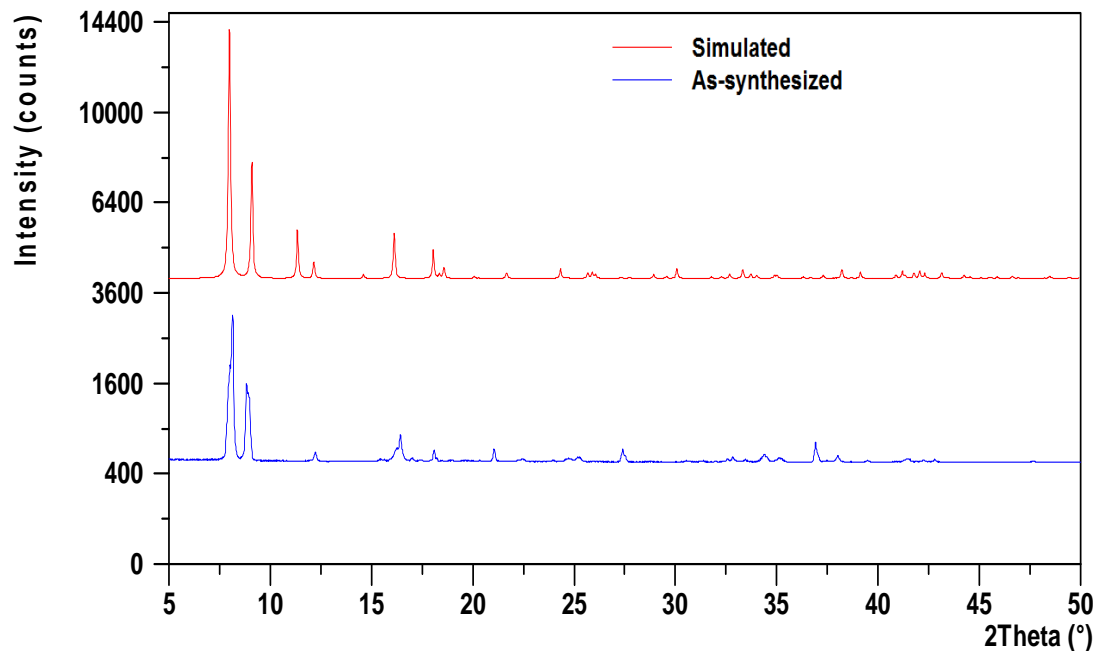


Figure S1: Comparison of PXRD pattern for as-synthesized Zn-1,4-NDC-DABCO or DMOF-N and its theoretical pattern from single crystal data

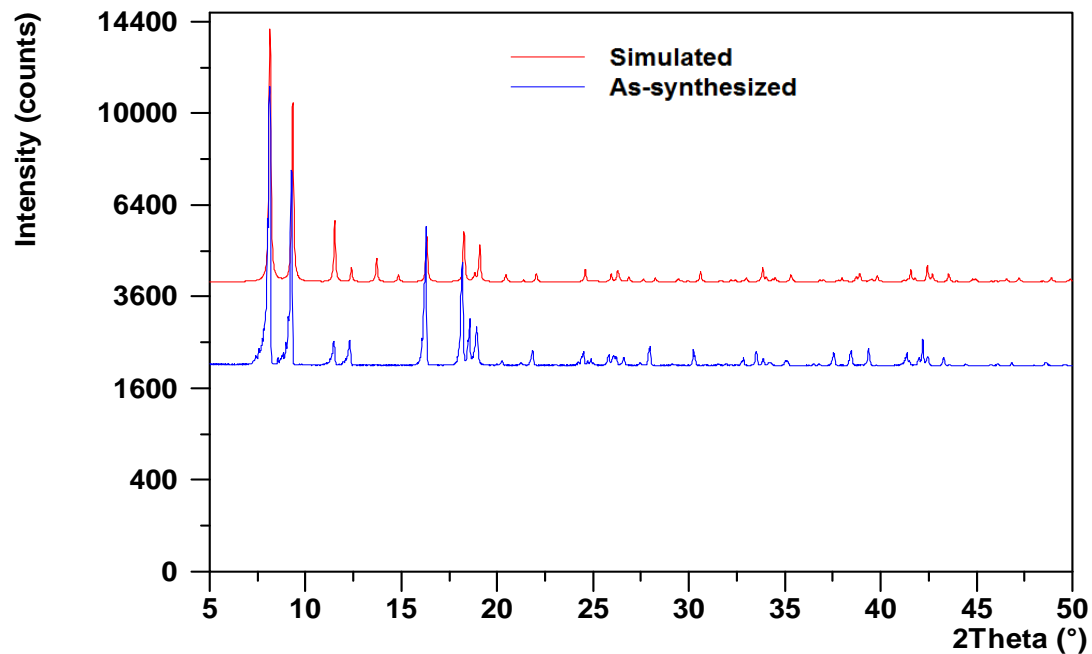


Figure S2: Comparison of PXRD pattern for as-synthesized Zn-ADC-DABCO or DMOF-A and its theoretical pattern from single crystal data

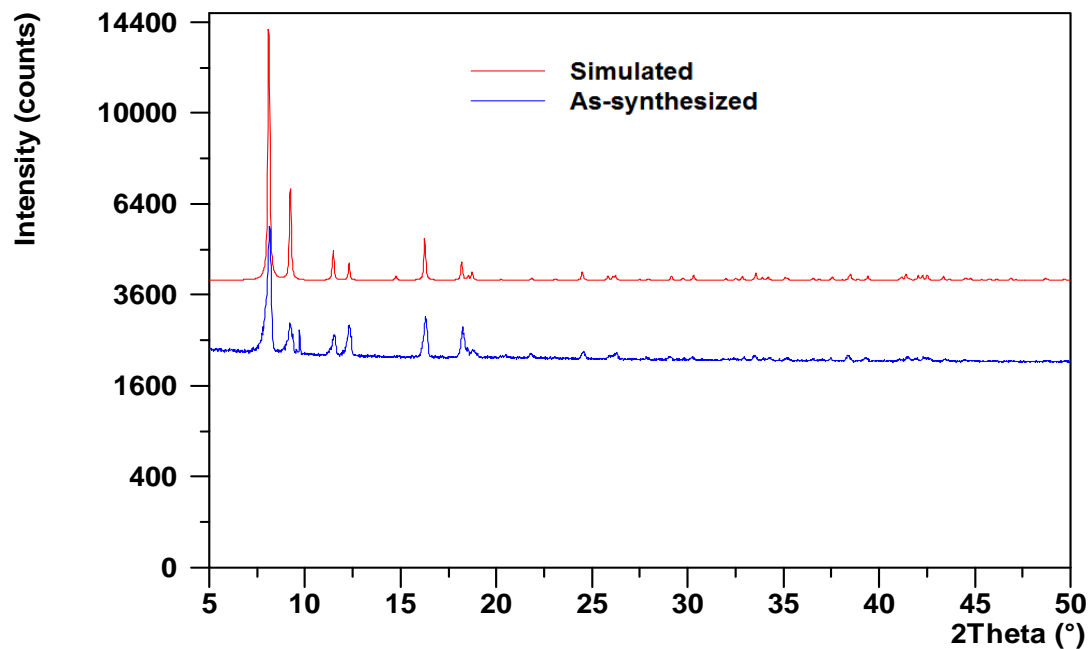


Figure S3: Comparison of PXRd pattern for as-synthesized Zn-BDC-TMBDC-DABCO or DMOF-TM1 and its theoretical pattern from single crystal data

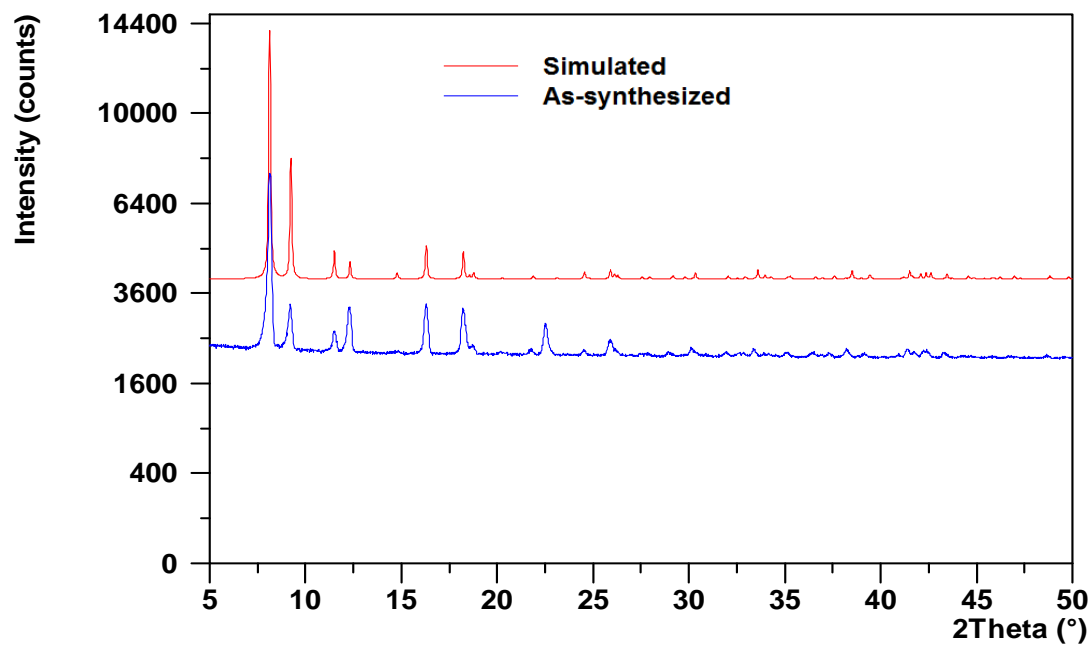


Figure S4: Comparison of PXRd pattern for as-synthesized Zn-TMBDC-DABCO or DMOF-TM2 and its theoretical pattern from single crystal data

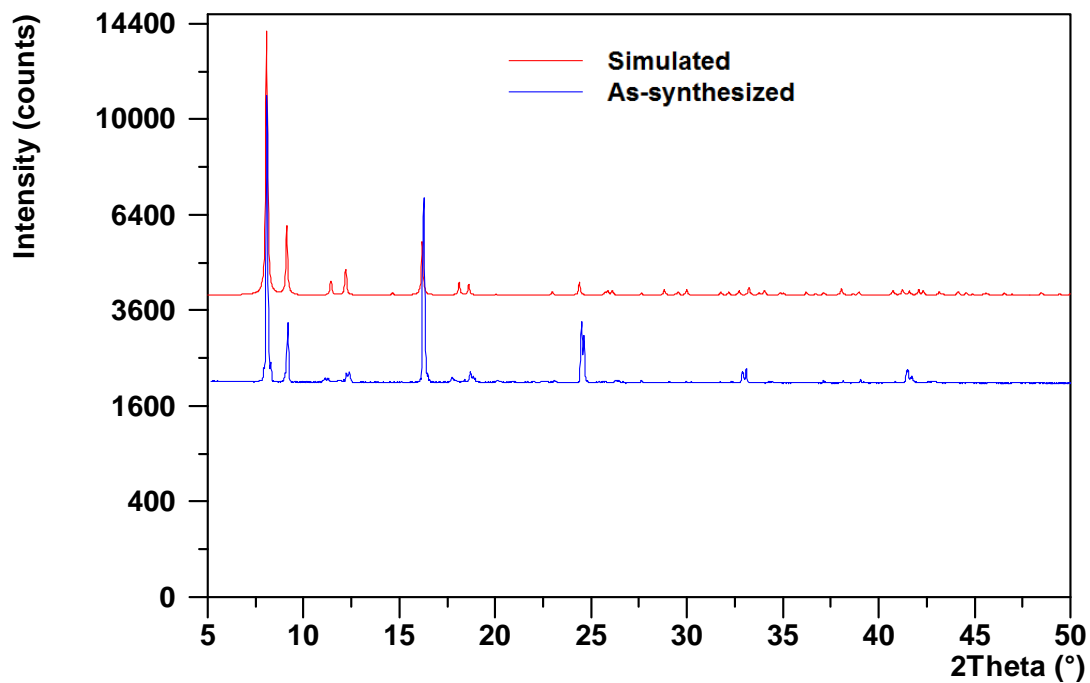


Figure S5: Comparison of PXR D pattern for as-synthesized Zn-BDC-NO<sub>2</sub>-DABCO or DMOF-NO<sub>2</sub> and its theoretical pattern from single crystal data

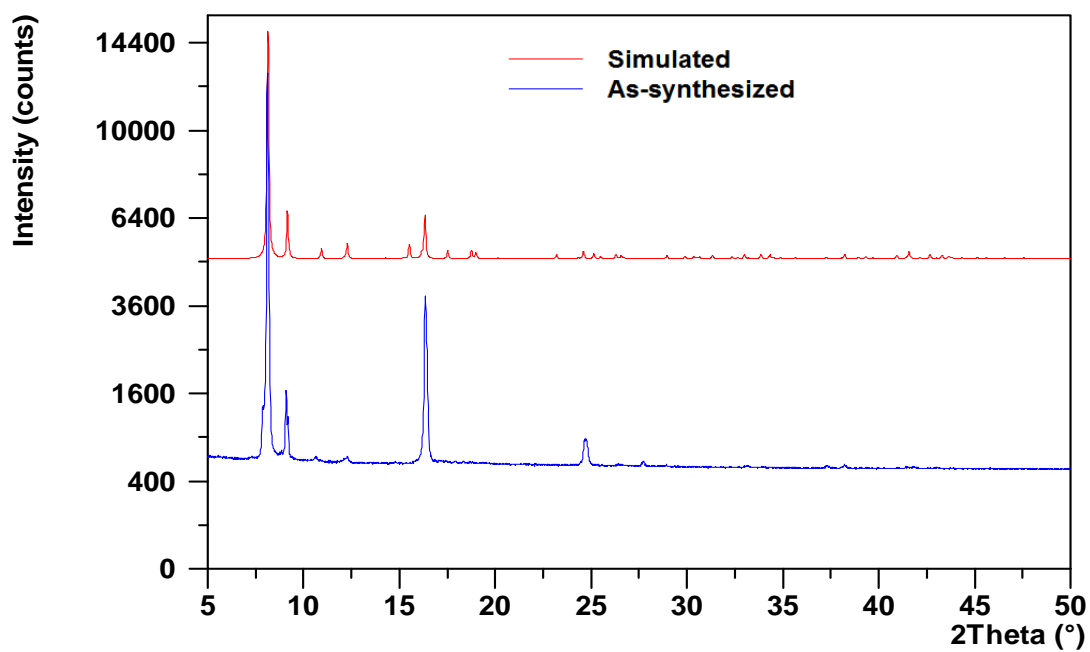


Figure S6: Comparison of PXR D pattern for as-synthesized Zn-BDC-Br-DABCO or DMOF-Br and its theoretical pattern from single crystal data

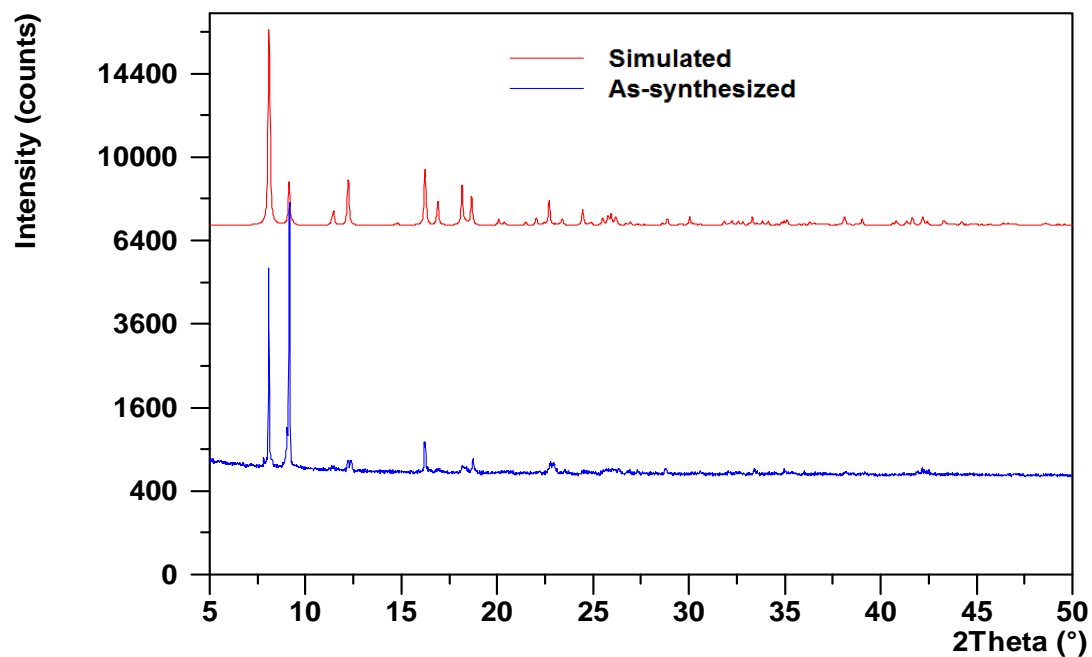


Figure S7: Comparison of PXRD pattern for as-synthesized Zn-BDC-Cl<sub>2</sub>-DABCO or DMOF-Cl<sub>2</sub> and its theoretical pattern from single crystal data

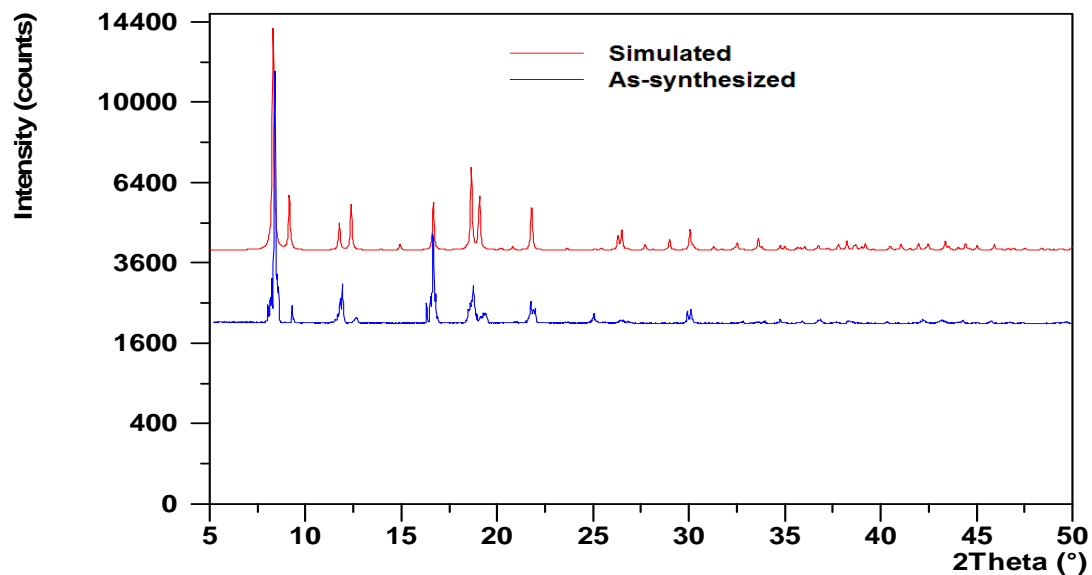


Figure S8: Comparison of PXRD pattern for as-synthesized Zn-BDC-OH-DABCO or DMOF-OH and its theoretical pattern from single crystal data

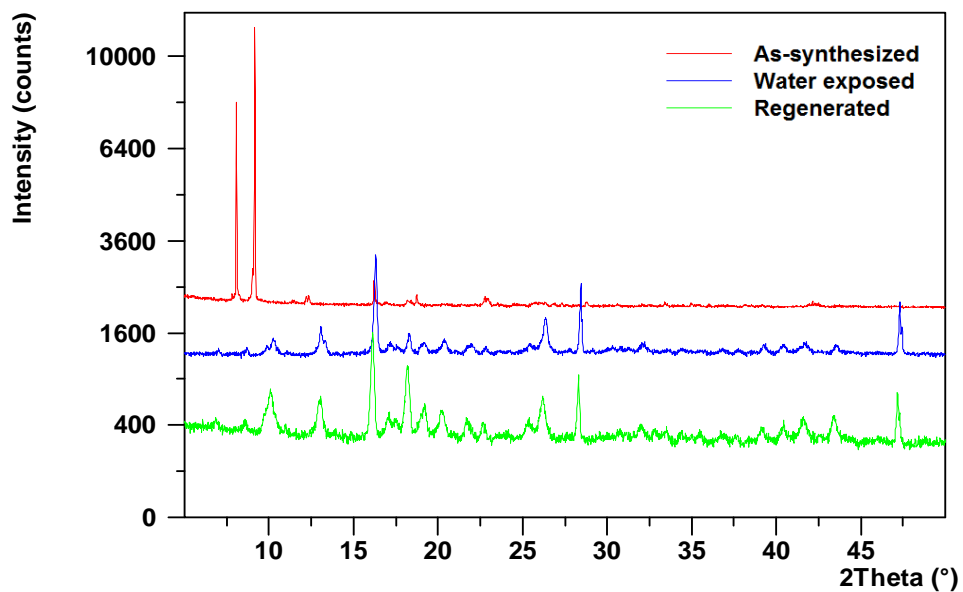
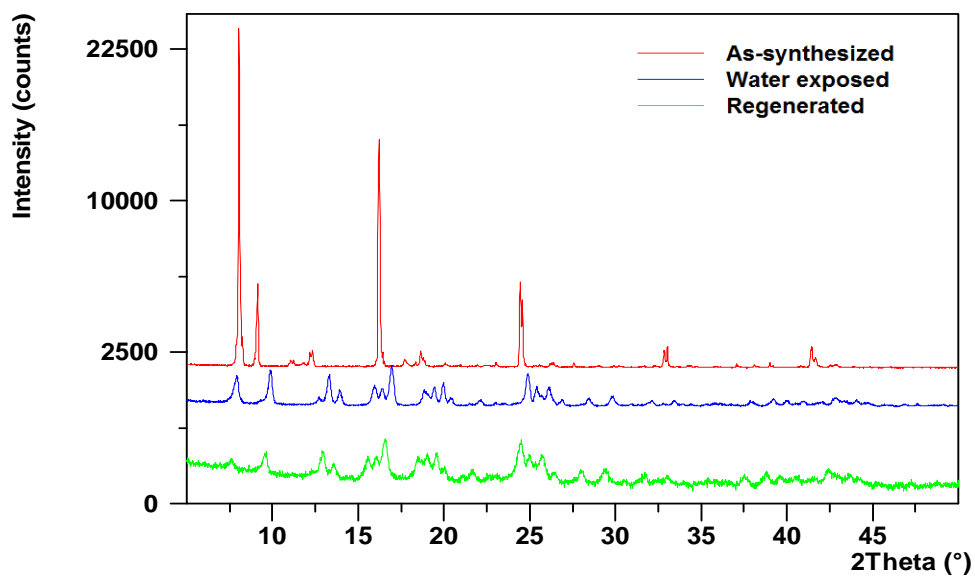


Figure S9. PXRD patterns for as-synthesized, water-exposed (up to 90% RH), and regenerated a) DMOF-NO<sub>2</sub> (top) and b) DMOF-Cl<sub>2</sub> (bottom).

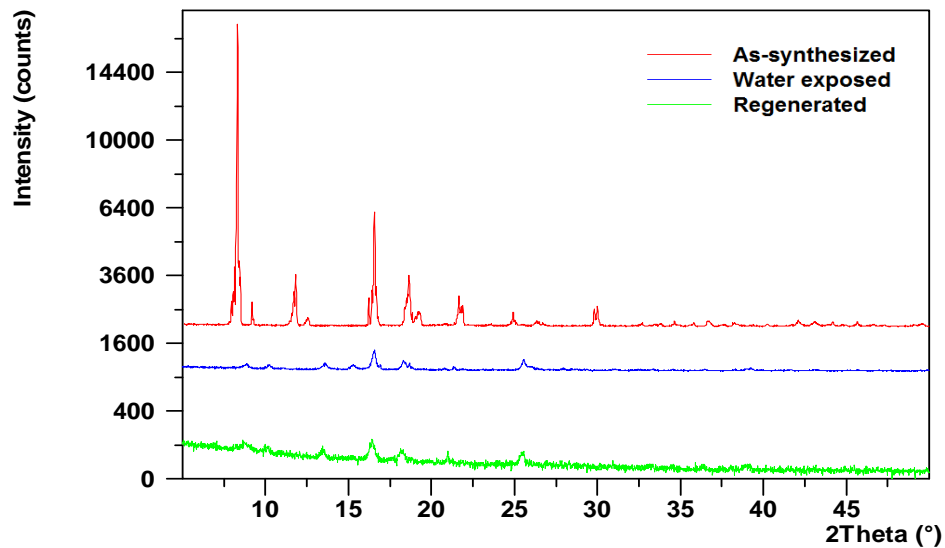


Figure S10. PXRD patterns for as-synthesized, water-exposed (up to 90% RH), and regenerated DMOF-OH.

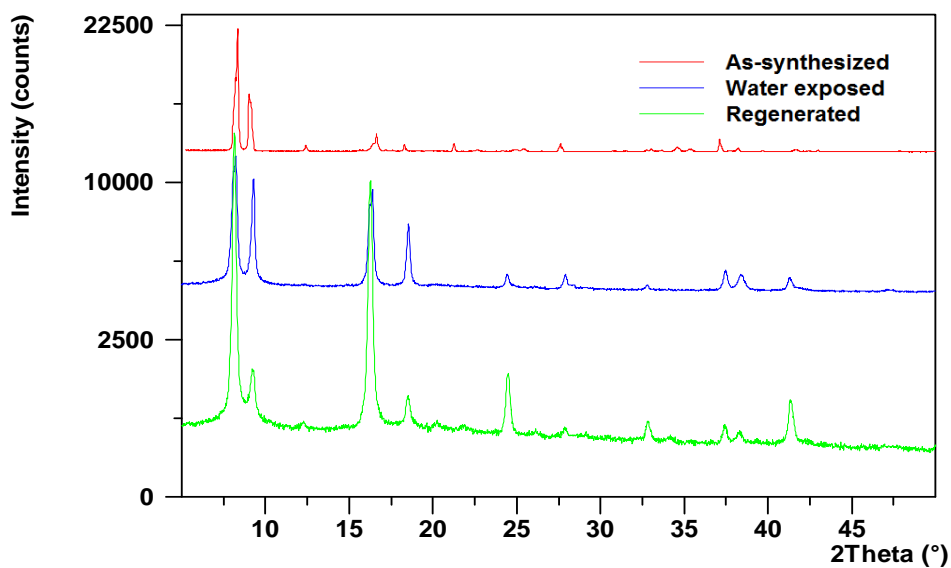


Figure S11. PXRD patterns for as-synthesized, water-exposed (up to 90% RH), and regenerated DMOF-N.

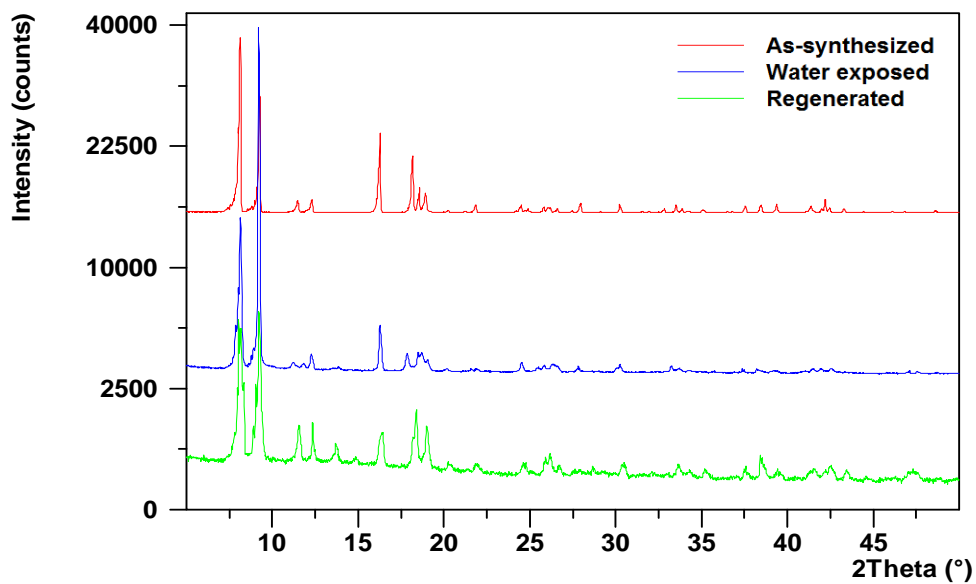


Figure S12. PXRD patterns for as-synthesized, water-exposed (up to 90% RH), and regenerated DMOF-A.

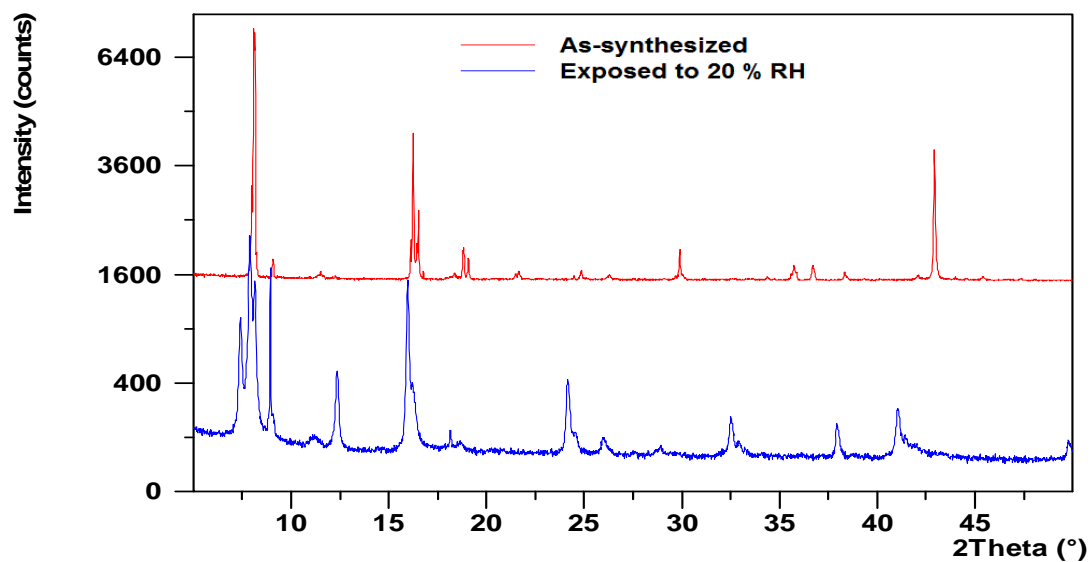


Figure S13: PXRD patterns for as-synthesized, and water exposed (only up to 20% RH) Zn-BDC-OH-DABCO or DMOF-OH

## 2.2 Surface Area Analysis

Specific surface areas were determined by applying the BET model to nitrogen adsorption isotherms measured at 77 K for each activated MOF before and after water exposure using a Quadrasorb system from Quantachrome Instruments. It should be noted that surface area values for the same MOF may differ in various publications due to lack of consistency on the pressure range used to fit the BET model. Here, the BET theory was applied over the pressure range determined using the method of Walton et al.<sup>[1a]</sup>, which typically leads to analysis in the low pressure range ( $P/P_0 < 0.05$ ). The nitrogen adsorption isotherms obtained after solvent removal from as-synthesized MOFs showed typical Type I behavior according to the IUPAC classification<sup>[1b]</sup> (Figs. S14-S21).

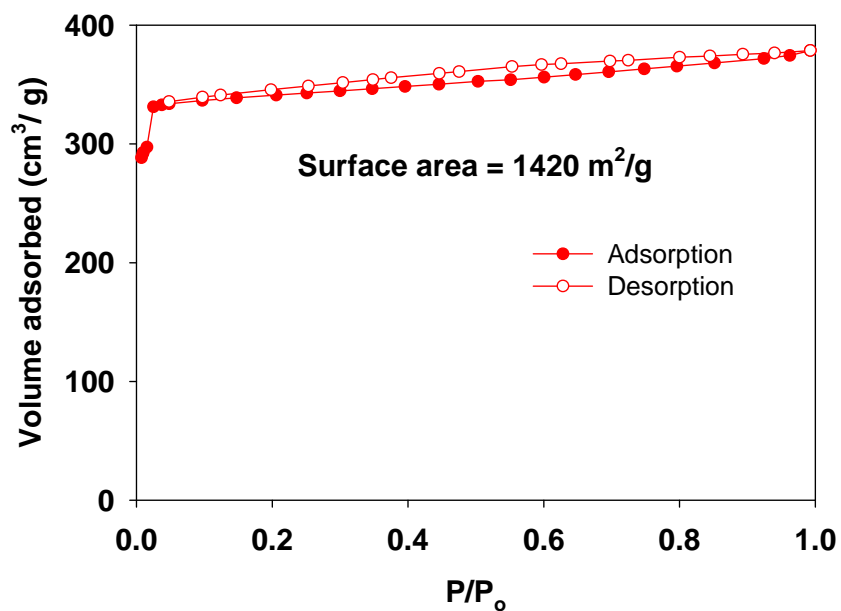


Figure S14: Nitrogen isotherm of activated Zn-1,4-NDC-DABCO or DMOF- N at 77 K (closed symbols – adsorption, open symbols – desorption)

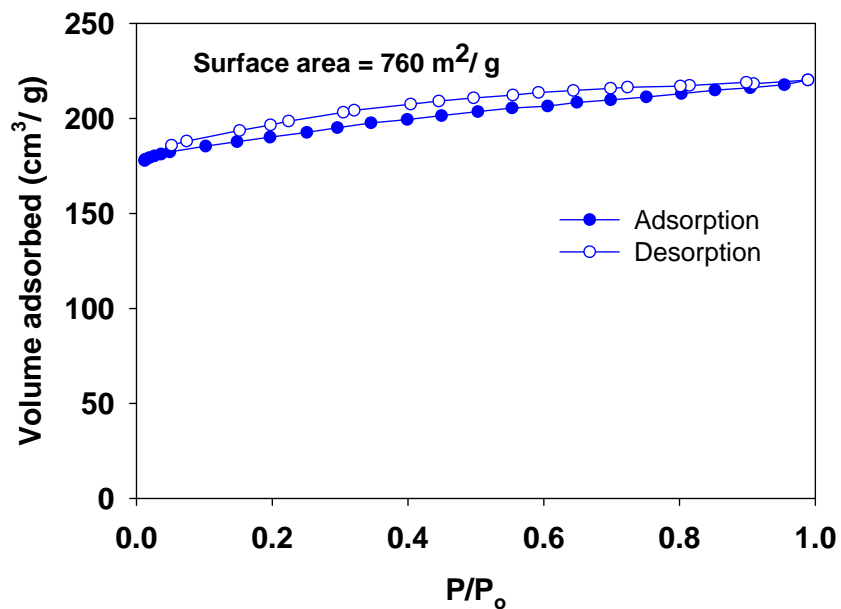


Figure S15: Nitrogen isotherm of activated Zn-ADC-DABCO or DMOF- A at 77 K (closed symbols – adsorption, open symbols – desorption)

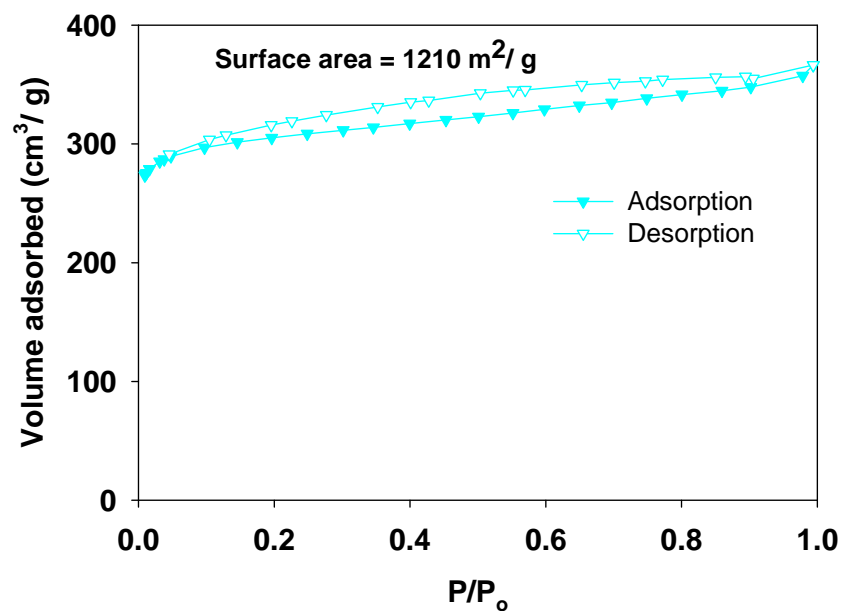


Figure S16: Nitrogen isotherm of activated Zn-BDC-TMBDC-DABCO or DMOF- TM1 at 77 K (closed symbols – adsorption, open symbols – desorption)

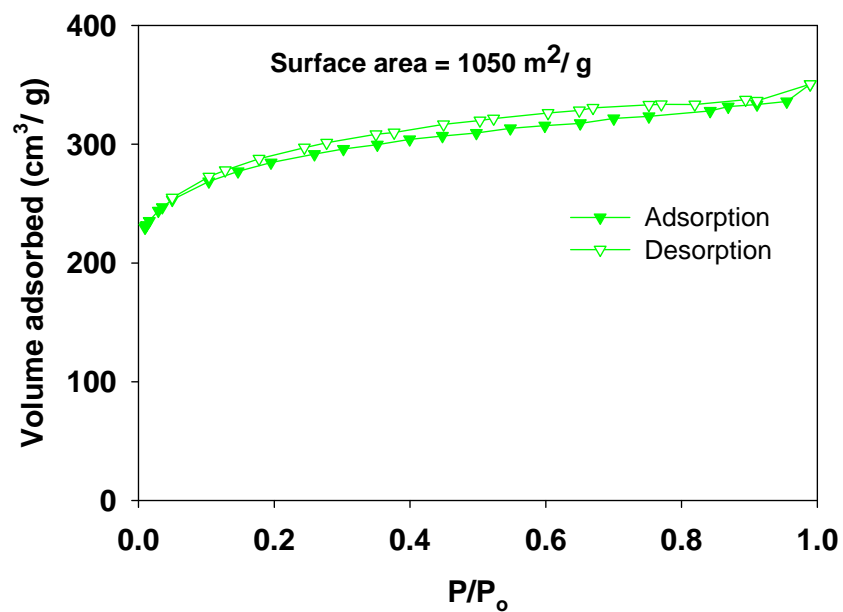


Figure S17: Nitrogen isotherm of activated Zn-TMBDC-DABCO or DMOF- TM2 at 77 K (closed symbols – adsorption, open symbols – desorption)

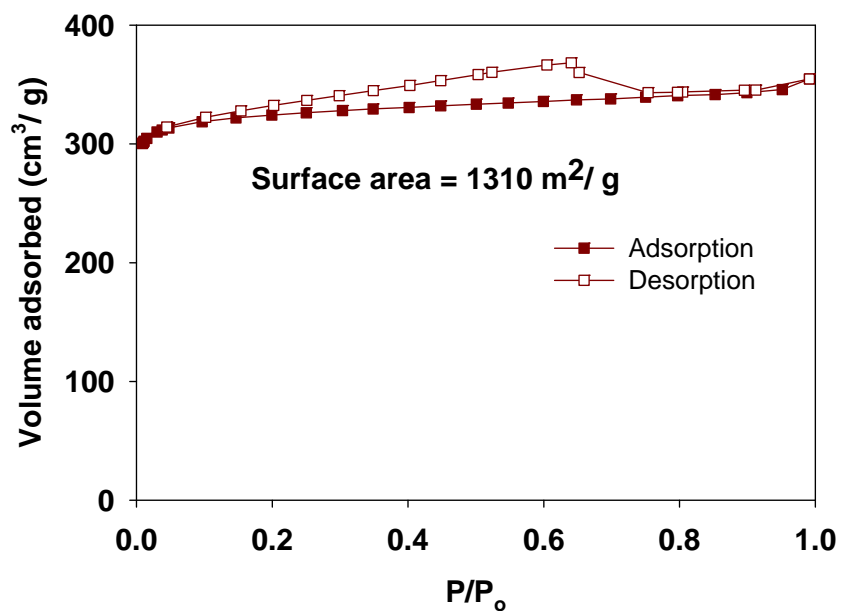


Figure S18: Nitrogen isotherm of activated Zn-BDC-NO<sub>2</sub>-DABCO or DMOF- NO<sub>2</sub> at 77 K (closed symbols – adsorption, open symbols – desorption)

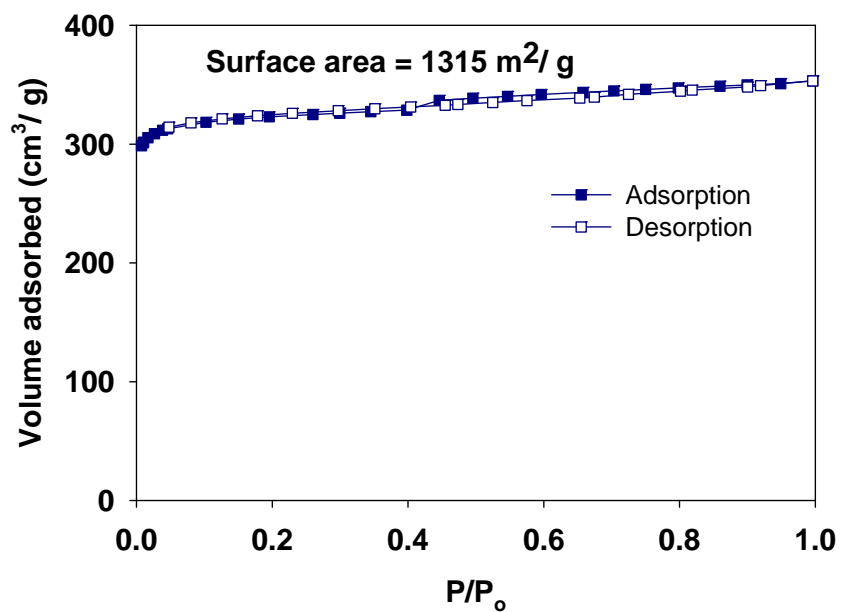


Figure S19: Nitrogen isotherm of activated Zn-BDC-Br-DABCO or DMOF- Br at 77 K (closed symbols – adsorption, open symbols – desorption)

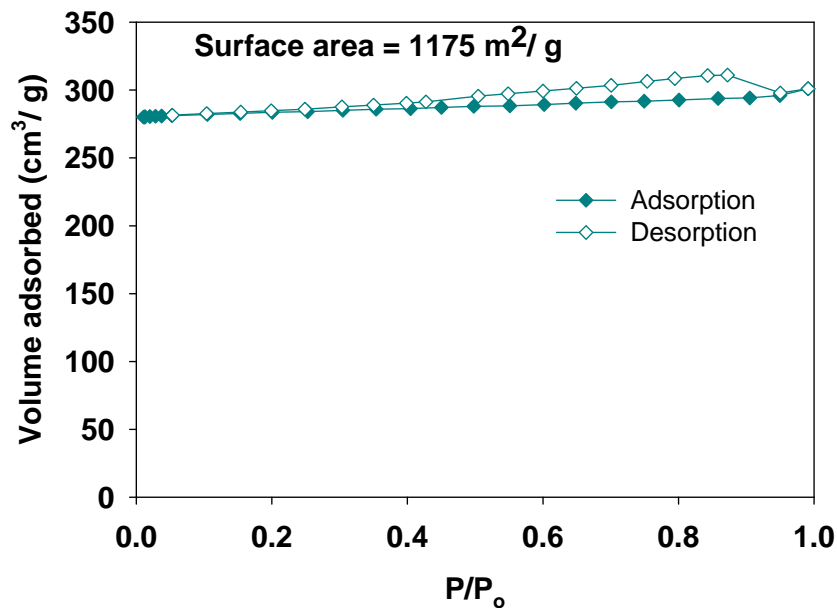


Figure S20: Nitrogen isotherm of activated Zn-BDC-Cl<sub>2</sub>-DABCO or DMOF- Cl<sub>2</sub> at 77 K (closed symbols – adsorption, open symbols – desorption)

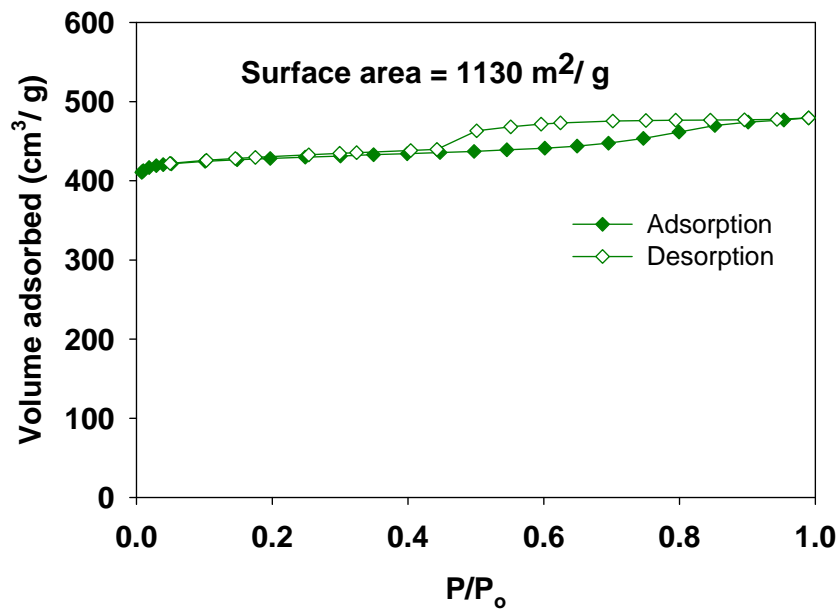


Figure S21: Nitrogen isotherm of activated Zn-BDC-OH-DABCO or DMOF- OH at 77 K (closed symbols – adsorption, open symbols – desorption)

### 2.3 Water Vapor Adsorption Isotherm Measurements

Water vapor adsorption isotherms were obtained using an Intelligent Gravimetric Analyzer (IGA-3 series, Hiden Analytical Ltd.). Dry air was used as the carrier gas, with a portion being effervesced through a canister filled with deionized water. The ratio of saturated air and dry air was changed using two mass flow controllers to control the relative humidity (RH). Due to water condensation in the equipment at higher humidities, experiments were conducted only up to 90% RH. The total gas flow rate was set at 200 cc/min for all the experiments, and each adsorption/desorption step was given sufficient time to approach equilibrium for all RH points. Typical equilibrium times ranged from 15 minutes to 20 hrs. Before starting the adsorption measurement, the sample was heated under vacuum at the activation temperatures of the samples given in Table S2 until no further weight loss was observed.

Table S1: Loss of surface area of isostructural pillared MOFs (DMOF-X) after water exposure

Material	Pore	Pore	Surface Area* (m <sup>2</sup> /g)		
	Volume <sup>†</sup> (cm <sup>3</sup> /g)	Diameter (c, a, b) <sup>‡</sup> (Å)	Before	After <sup>§</sup>	% Loss
<sup>[6]</sup> DMOF	0.75	7.5x7.5,4.8x3.2,4.8x3.2	1980	7	100
DMOF-N	0.57	5.7, -, -	1420	1050	26
DMOF-A	0.33	-,4.8x3.2,4.8x3.2	760	726	4
DMOF-TM1	0.53	3.5-7.5, -, -	1210	822	32
DMOF-TM2	0.51	3.5, -, -	1050	1050	0
DMOF-NO <sub>2</sub>	0.53	6.2x4.3, -, -	1310	38	97
DMOF-Br	0.53	5.0x2.0, -, -	1315	1	100
DMOF-Cl <sub>2</sub>	0.45	3.8x3.8, -, -	1175	1	100
DMOF-OH	0.54	7.5x7.5,4.7x3.2, 4.7x3.2	1130	2	100

<sup>†</sup>Obtained from the Dubinin-Astakov model of N<sub>2</sub> adsorption at 77K

<sup>‡</sup>Obtained from literature<sup>[2-6]</sup>

\*BET Analysis<sup>[1a]</sup>

<sup>§</sup>After 90% RH exposure

Table S2: Comparison of properties of isostructural pillared MOFs (DMOF-X)

Material	Activation process (under vacuum)	Thermal Stability <sup>‡</sup> (°C)
DMOF	110 °C (12 h)	300
DMOF-N	25 °C (12h) <sup>#</sup>	320
DMOF-A	120 °C (12 h)	350
DMOF-TM1	110 °C (12 h)	320
DMOF-TM2	110 °C (12 h)	320
DMOF-NO <sub>2</sub>	110 °C (12 h)	300
DMOF-Br	110 °C (12 h)	300
DMOF-Cl <sub>2</sub>	110 °C (12 h)	300
DMOF-OH	110 °C (12 h)	300

<sup>‡</sup> Obtained from literature<sup>[2-6]</sup>

<sup>#</sup> Solvent exchange with chloroform

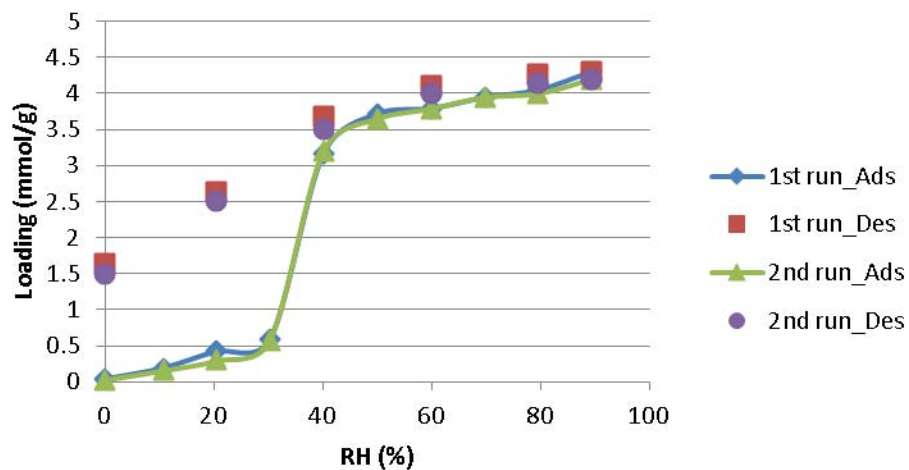


Figure S22: Water vapor adsorption isotherms at 25C for DMOF-CI2 measured on two samples from the same batch.

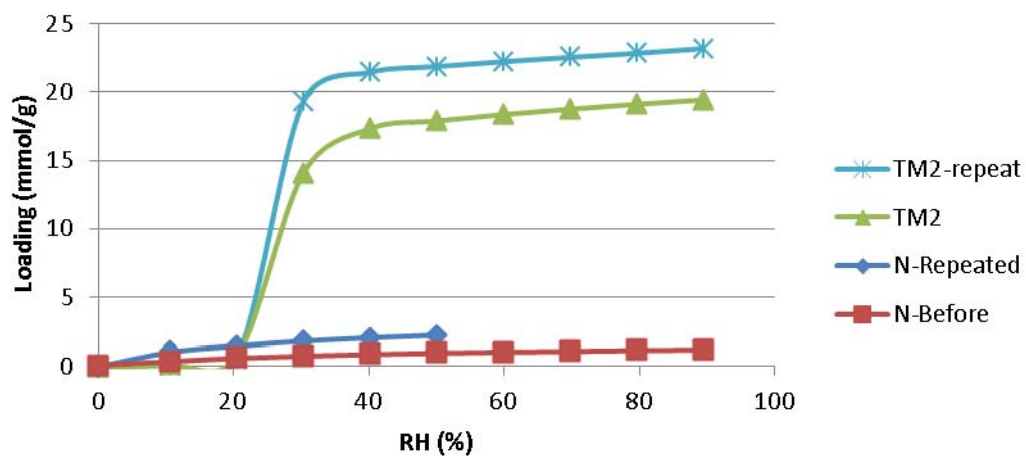


Figure S23: Water vapor adsorption isotherms at 25C for DMOF-TM2 and DMOF-N measured on two samples from different batches.

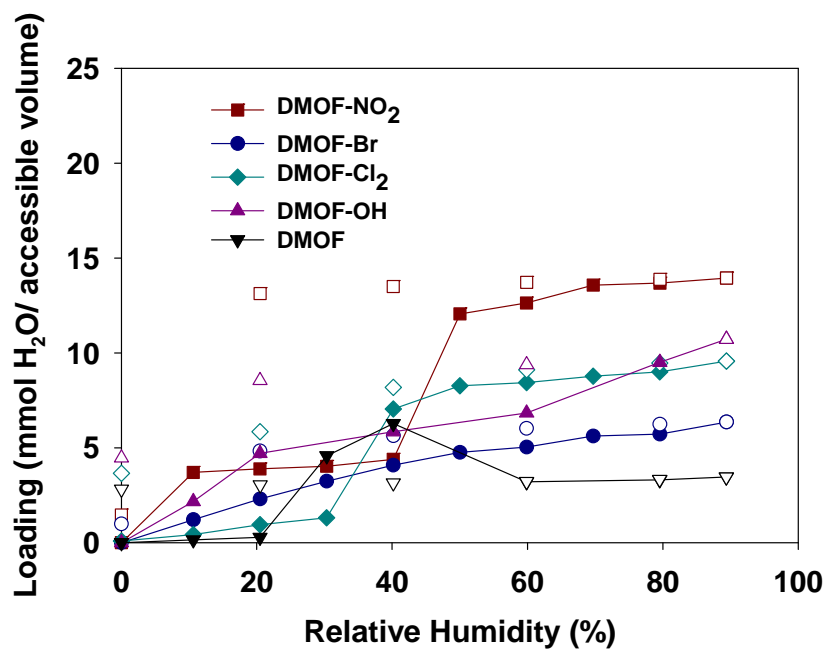


Figure S24: Water adsorption isotherms plotted on a pore volume basis ( $\text{cm}^3$ ) for DMOF with polar functional groups.

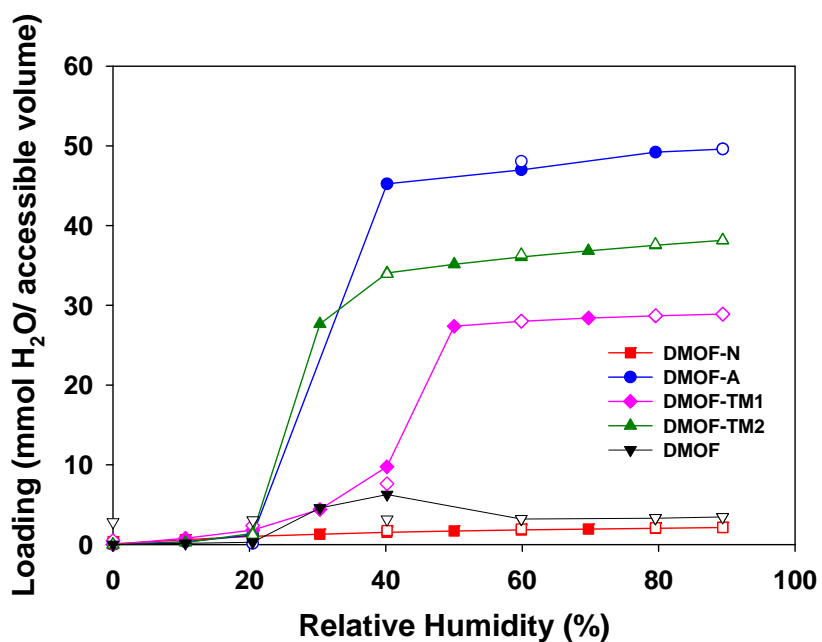


Figure S25: Water adsorption isotherms plotted on a pore volume basis ( $\text{cm}^3$ ) for DMOF with non-polar functional groups.

## References:

- [1] a) K. S. Walton, R. Q. Snurr, *J. Am. Chem. Soc.* **2007**, *129*, 8552-8556. b) S. Kitagawa, R. Kitaura, S. Noro, Functional porous coordination polymers. *Angew. Chem., Int. Ed.* **2004**, *43*(18), 2334-2375.
- [2] a) H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. – Eur. J.* **2005**, *11* (12), 3521-3529 ; b) D. Tanaka, S. Horike, S. Kitagawa, M. Ohba, M. Hasegawa, Y. Ozawa, K. Toriumi, *Chem. Commun.* **2007**, (30), 3142-3144.
- [3] K. Uemura, F. Onishi, Y. Yamasaki, H. Kita, *J. Solid State Chem.* **2009**, *182* (10), 2852-2857.
- [4] K. Uemura, Y. Yamasaki, F. Onishi, H. Kita, M. Ebihara, *Inorganic Chemistry* **2010**, *49* (21), 10133-10143.
- [5] Chen, Z.; Xiang, S.; Arman, H. D.; Li, P.; Zhao, D.; Chen, B., *Eur. J. Inorg. Chem.* **2011**, *2011* (14), 2227-2231.
- [6] a) Y. G. Zhao, H. H. Wu, T. J. Emge, Q. H. Gong, N. Nijem, Y. J. Chabal, L. Z. Kong, D. C. Langreth, H. Liu, H. P. Zeng, J. Li, *Chem.- Eur. J.* **2011**, *17* (18), 5100-5108; b) D. Tanaka, M. Higuchi, S. Horike, R. Matsuda, Y. Kinoshita, N. Yanai, S. Kitagawa, *Chem.- Asian J.* **2008**, *3* (8-9), 1343-1349.