

Room Temperature Synthesis of Metal-Organic Framework Isomers in the Tetragonal and Kagome Crystal Structure

Julian Hungerford and Krista S. Walton*

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive NW,
Atlanta, Georgia 30332, USA

Supplemental Information

Materials and Crystal Structure

A series of functionalized DMOF-1 materials were synthesized via a fast room temperature synthesis procedure. The parent ligand for DMOF-1, terephthalic acid (BDC), is shown below. The other ligands used in this study are also shown below: dimethyl terephthalic acid (DM), 2-aminoterephthalic acid (NH_2), 2,3,5,6-tetramethyl terephthalic acid (TM), and anthracene dicarboxylic acid (ADC). The formed materials will be referred to as DMOF-DM, DMOF- NH_2 , DMOF-TM, and DMOF-ADC respectively. A solvents property table for the solvents used in the synthesis of DMOF and ZnBD is also provided in Table S1.

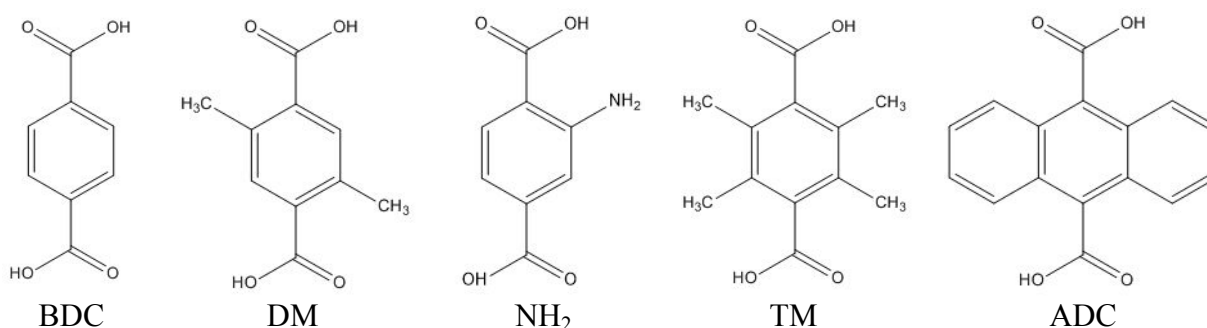


Figure S1: Ligands in DMOF and ZnBD Room Temperature Synthesis

The structures of DMOF-1 and ZnBD are shown in Figure S2. DMOF-1 has tetragonal crystal structure and has a $7.5 \text{ \AA} \times 7.5 \text{ \AA}$ pore window in the BDC ligand plane. ZnBD has a Kagome crystal structure and has two pore windows in the BDC ligand plane. The smaller pore is triangular in shape and can fit a circle of diameter 4.5 \AA within this pore. The larger pore is hexagonal and measures 15 \AA from one end to the other. Table S2 summarizes the BET surface areas, pore sizes, and pore volumes of the DMOF-1 (including functionalized forms with DM, TM, and ADC) and ZnBD MOFs.¹⁻⁵



Figure S2: Crystal structure of DMOF-1 (left) and ZnBD (right). “Reproduced from 5. Copyright 2017, Elsevier.”

Table S1: Solvent Properties^{6,7,8}

Solvent	Dielectric Constant	Density (g/ml)	Dipole Moment (D)	Boiling Point (°C)	MOF Formed
Acetone	20.7	0.788	2.85	56	DMOF-1
Acetonitrile	37.5	0.782	3.45	82	DMOF-1
DEF	29.02	0.910	3.93	176	DMOF-1
DMF	36.7	0.945	3.86	152	ZnBD
DMSO	46.7	1.096	3.9	189	ZnBD
Ethanol	24.5	0.789	1.69	78	DMOF-1
Methanol	32.7	0.791	1.7	65	DMOF-1

Table S2: BET SA, pore volume, and pore sizes for the DMOF-1 and ZnBD MOFs¹⁻⁵

MOF	BET SA (m ² /g)	Pore Volume (cm ³ /g)	Pore Size(s) (Å)
DMOF-1	1980	0.75	7.5 x 7.5
DMOF-TM	1050	0.5	3.5 x 3.5
DMOF-DM	1115	0.51	5.8 x 5.8
DMOF-ADC	760	0.33	3.75 x 3.75
ZnBD	2000-2400	0.8	4.5; 15 (diameter)

Brunauer-Emmett-Teller (BET) Surface Area Analysis

Nitrogen physisorption analysis was used to assess the pore volumes and surface areas of the synthesized materials. Table 1 in the main text shows the results of those experiments and Figures S3 – S5 show the nitrogen physisorption isotherms that were collected at 77 K.

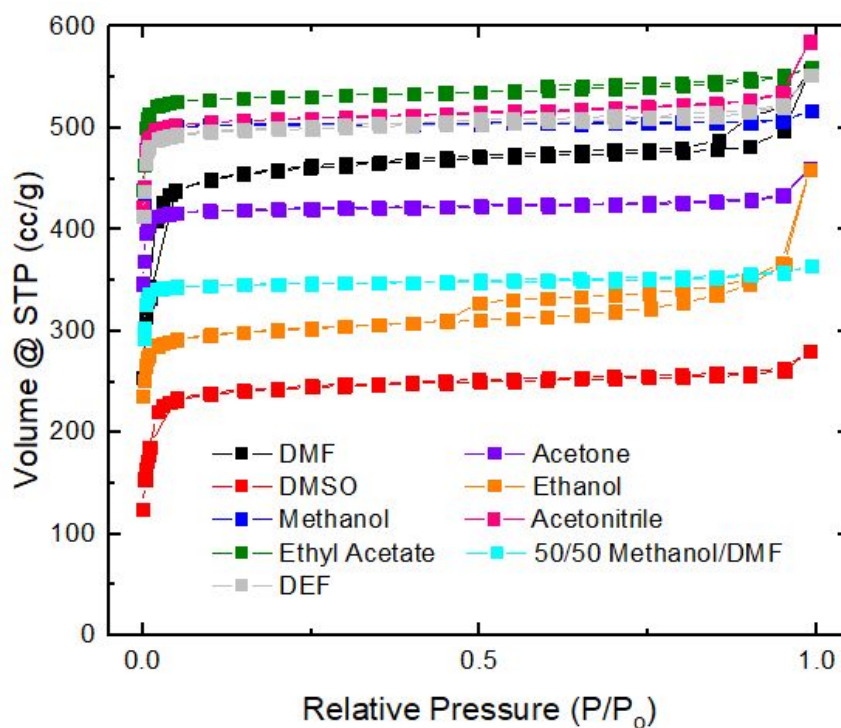


Figure S3: Nitrogen physisorption isotherms for ZnBD and DMOF samples synthesized using a variety of solvents (DMF = N,N-dimethylformamide, DMSO = dimethyl sulfoxide, methanol, ethyl acetate, DEF = N,N-diethylformamide, acetone, ethanol, acetonitrile, 50/50 methanol/DMF)

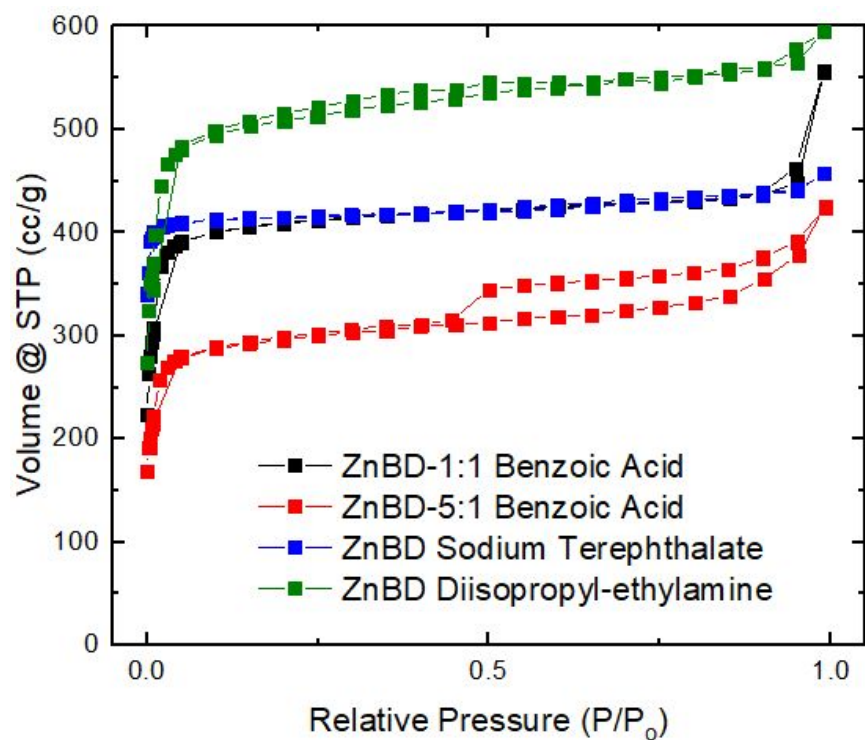


Figure S4: Nitrogen physisorption isotherms for ZnBD samples synthesized using a variety of acid and base modulators (1:1 Benzoic acid/BDC, 5:1 Benzoic acid/BDC, Sodium terephthalate, diisopropyl-ethylamine)

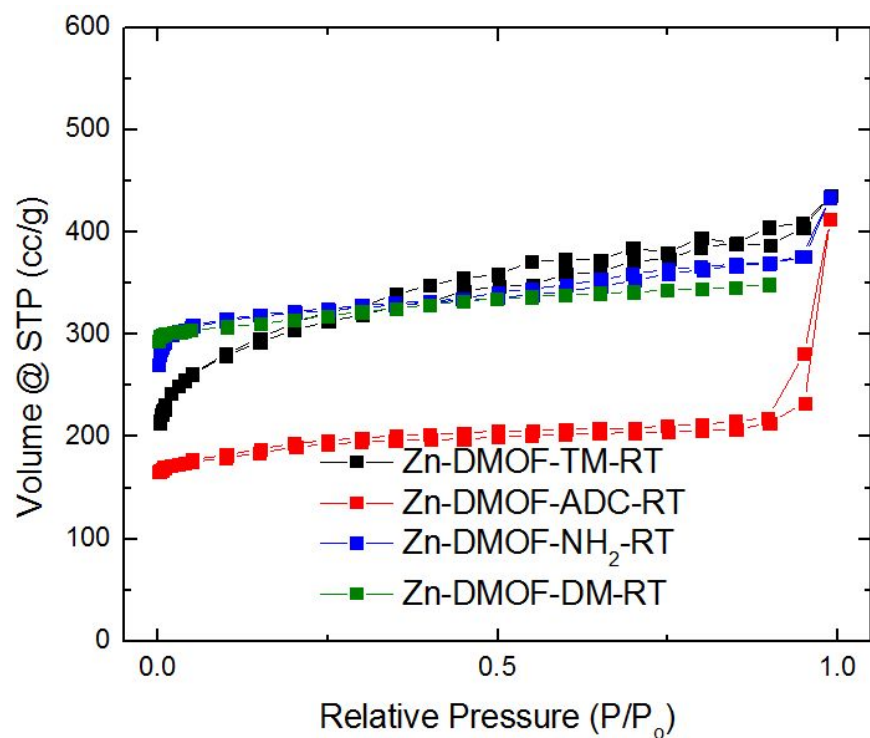


Figure S5: Nitrogen physisorption isotherms for Zn-DMOF-X samples synthesized at room temperature in DMF. (DM = 2,5-dimethylterephthalic acid, NH₂ = 2-aminoterephthalic acid, TM = 2,3,5,6-tetramethylterephthalic acid, and ADC = 9,10-anthracenedicarboxylic acid)

CO₂ Adsorption Comparison

Figure S6 shows a comparison of the CO₂ adsorption isotherms between the ZnBD-DMF, Zn-DMOF-Methanol, Zn-DMOF-Ethanol, and Zn-DMOF synthesized by Liang et. al.⁹ There is essentially complete overlap between the Zn-DMOF-Liang et. al. synthesized DMOF-1 and the DMOF-1 that we synthesized in methanol at room temperature. When ethanol was used as a solvent we see a slight decrease in the CO₂ adsorption, likely due to the decreased surface area and pore volume present in the material.

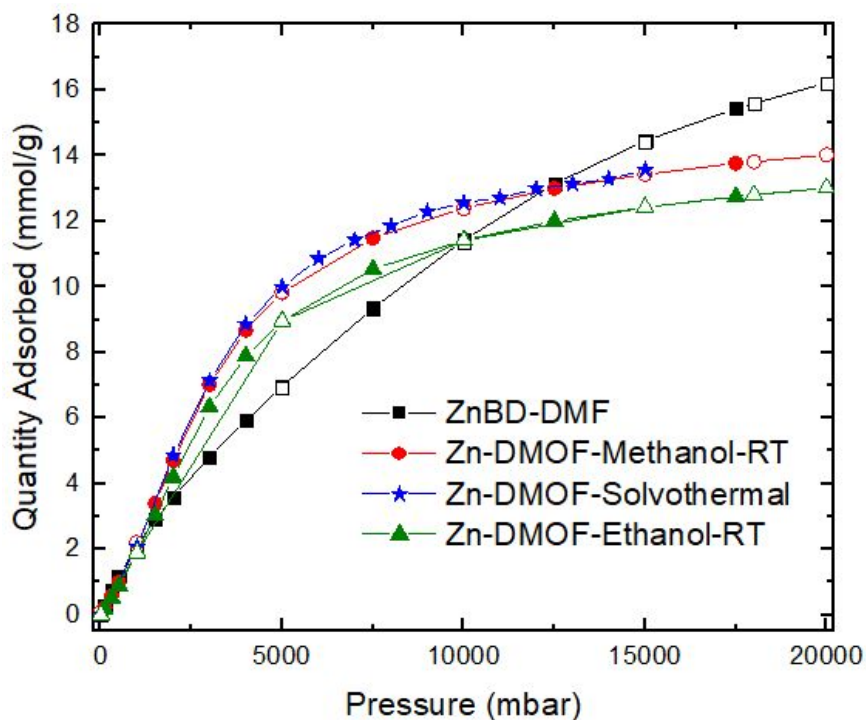


Figure S6: Comparison of the CO₂ adsorption isotherms for ZnBD-DMF, Zn-DMOF-Methanol-RT, Zn-DMOF-Ethanol-RT, and Zn-DMOF-Solvothermal. Data for Zn-DMOF-Solvothermal taken from 9.

Zn-DMOF-TM Stability

Zn-DMOF-TM has previously been reported as an air stable MOF for periods of up to one year.^{1,2} However, when synthesizing the material via room temperature synthesis methods we noted that the material broke down after a period of roughly 1 month as was evident by a loss in crystal structure, measured using PXRD and BET surface area analysis (Figure S7 and Table S3 respectively). We have been unable to identify the cause of this degradation and will be investigating it further in follow-up research.

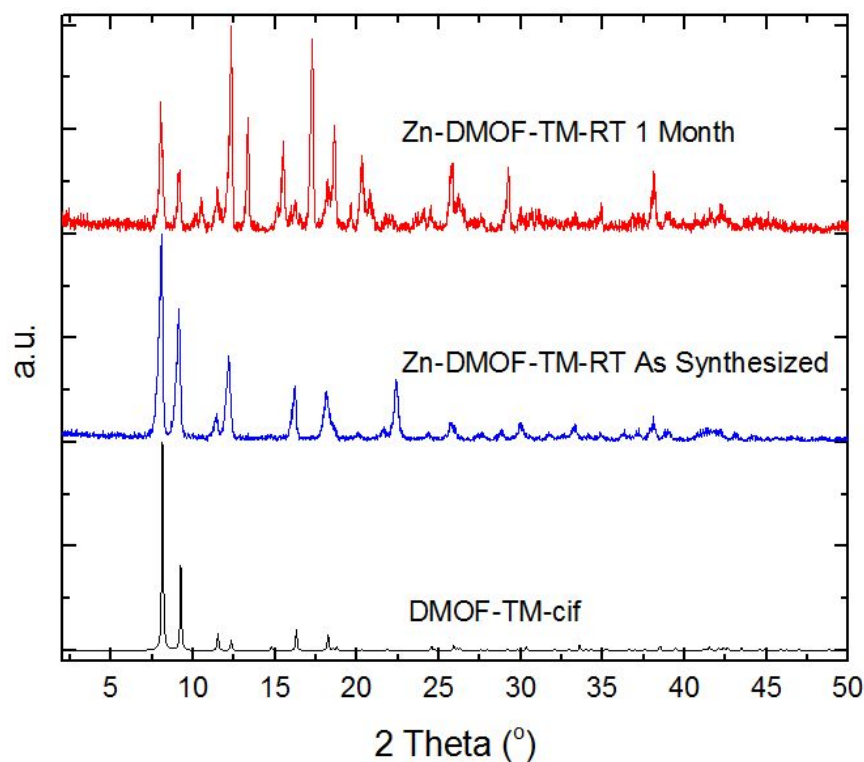


Figure S7: Zn-DMOF-TM PXRD patterns showing degradation after 1 month in air.

Table S3: BET surface area and pore volume of Zn-DMOF-TM-RT over time

MOF	BET SA (m ² /g)	Pore Volume (cm ³ /g)
Zn-DMOF-TM		
As Synthesized	950	0.434
1 month	265	0.122

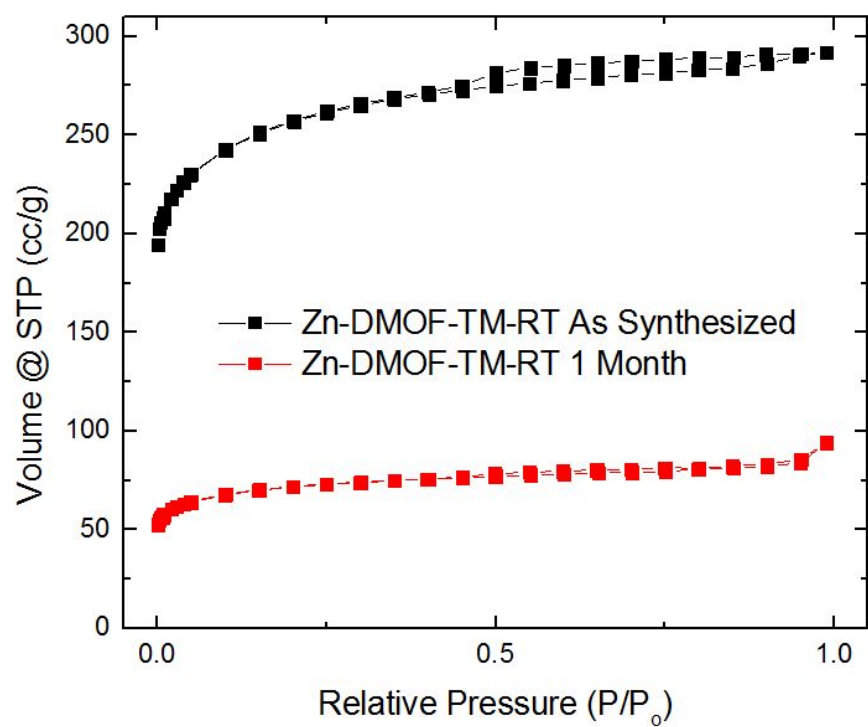


Figure S8: Nitrogen physisorption isotherms for Zn-DMOF-TM-RT over time

Metal Substitution Room Temperature Synthesis

Metal substitution in DMOF-1 has been successful for the following metal centers: zinc, cobalt, nickel, and copper.^{3,10,11} In this work we attempted to synthesize ZnBD, CoBD, NiBD, and CuBD using the room temperature synthesis procedure that was discussed in the main text of the manuscript. For all metal substitutions, metal nitrate salts were used as precursor materials and DMF was used as a solvent. Figure S9 shows the PXRD patterns of the resulting materials.

Figure S9 shows that we were successfully able to synthesize both ZnBD and CoBD, however after numerous trials we were unable to produce NiBD or CuBD. When conducting the room temperature synthesis using nickel salts we generally achieved an unidentified power pattern that does not match either the DMOF-1 or Kagome ZnBD lattice. It is also highly likely that the formed structure contains many phase impurities such that determination of its structure would be difficult. When using copper salts in the room temperature synthesis, a DMOF-1 phase persisted across multiple trials such that we were never able to produce a Kagome CuBD lattice. Table S4 shows the BET surface areas and pore volumes for the metal substituted $M_2(BDC)_2(DABCO)$ (Nitrogen physisorption isotherms are located in Figure S10). ZnBD-DMF and CoBD-DMF displayed similar surface areas (2100-2300 m²/g) and pore volumes (0.80 - 0.87 cm³/g) and Cu-DMOF-DMF had a slightly lower surface area (1871 m²/g) and pore volume (0.71 cm³/g).

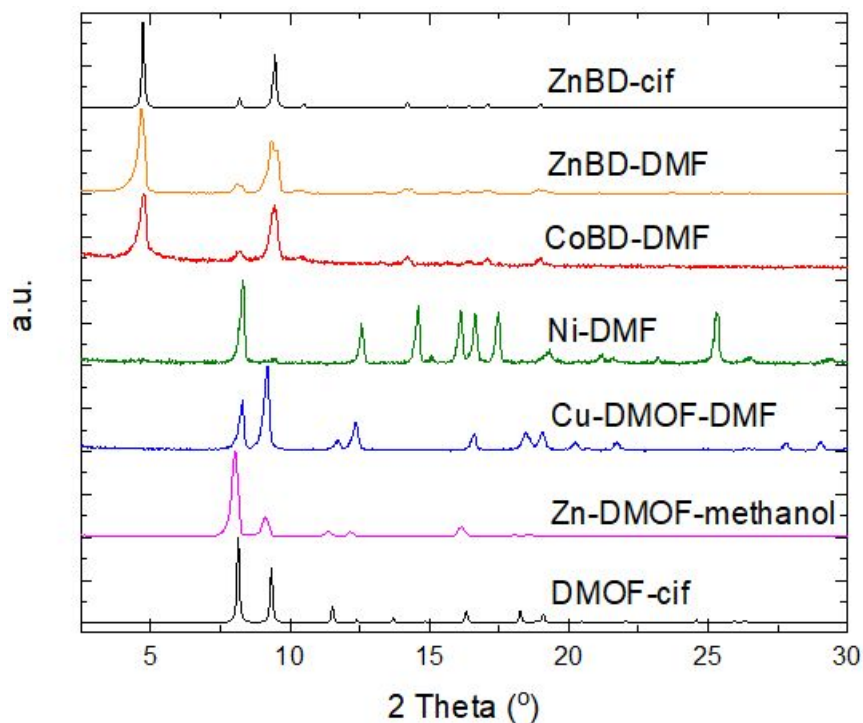


Figure S9: PXRD patterns of $M_2(BDC)_2(DABCO)$ where $M = \text{Zn, Co, Ni, Cu}$ all synthesized at room temperature in DMF.

Table S4: BET surface area and pore volume of $M_2(BDC)_2(DABCO)$ where $M = \text{Zn, Co, Ni, Cu}$ synthesized solvothermally in DMF.

MOF	BET SA (m^2/g)	Pore Volume cm^3/g
ZnBD-DMF	2104	0.80
CoBD-DMF	2281	0.86
Ni-DMF	NA	NA
Cu-DMOF-DMF	1871	0.71

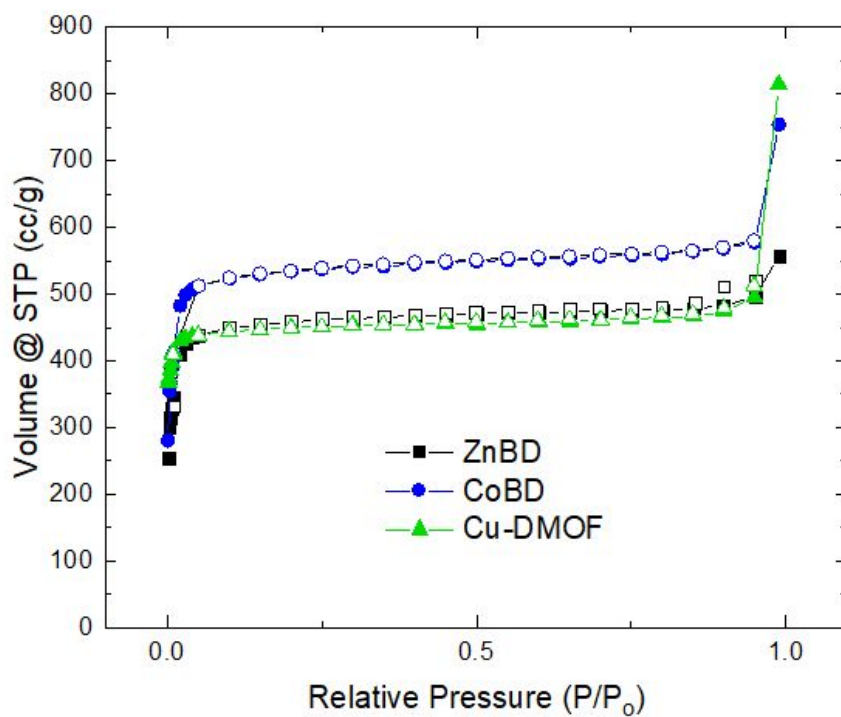


Figure S10: Nitrogen physisorption isotherms for ZnBD-DMF, CoBD-DMF, and Cu-DMOF-DMF synthesized at room temperature.

Investigation of Zinc Precursors in the Room Temperature Synthesis Procedure

In addition to $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which was used as the metal precursor throughout the main text, zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) and zinc chloride (ZnCl_2) were also explored as metal precursors. The PXRD patterns (Figure S11) and BET surface areas (Table S5 and nitrogen physisorption isotherms included in Figure S12) of the resultant materials are shown below.

DMOF-1 was formed in methanol for both metal precursors, zinc acetate and ZnCl_2 , see PXRD patterns in Figure S10. The surface areas of these materials were smaller than those obtained from the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ metal precursor used throughout the main text. The ZnCl_2 metal precursor in DMF did not form either of the expected structures and also resulted in a material with a very low surface area. Zinc acetate in DMF produced a combination of both frameworks, DMOF-1 and ZnBD, which can be observed in the PXRD patterns in Figure S11. This result suggests that the formation of the metal secondary building unit may also influence MOF topology and further experimentation would be required to completely understand the impact that metal salts have on directing MOF topology. We therefore recommend that when conducting room temperature synthesis of DMOF-1 or ZnBD that $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ be used as the preferred metal precursor.

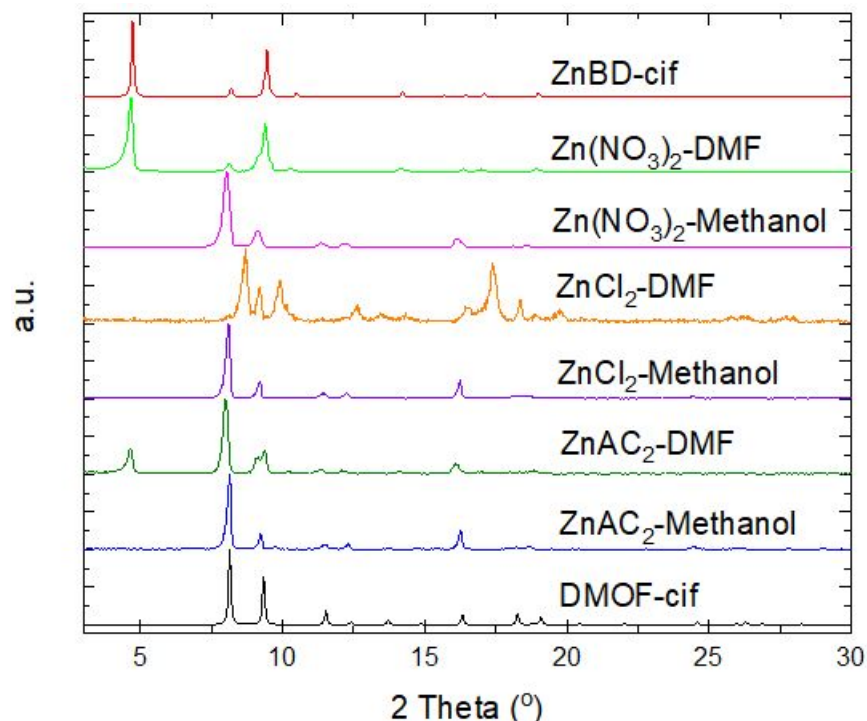


Figure S11: PXRD patterns of $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ synthesized from different metal precursors (zinc nitrate = $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, zinc chloride = ZnCl_2 , and zinc acetate = $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (AC_2)) using methanol and DMF as solvents

Table S5: BET surface area and pore volume of $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ synthesized from different metal precursors ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) using methanol and DMF as solvents

MOF	BET SA (m^2/g)	Pore Volume cm^3/g
$\text{Zn}(\text{NO}_3)_2$ -DMF	2104	0.80
$\text{Zn}(\text{NO}_3)_2$ -Methanol	2113	0.78
ZnCl_2 -DMF	50	0.03
ZnCl_2 -Methanol	1519	0.57
ZnAC_2 -DMF	1481	0.57
ZnAC_2 -Methanol	1704	0.64

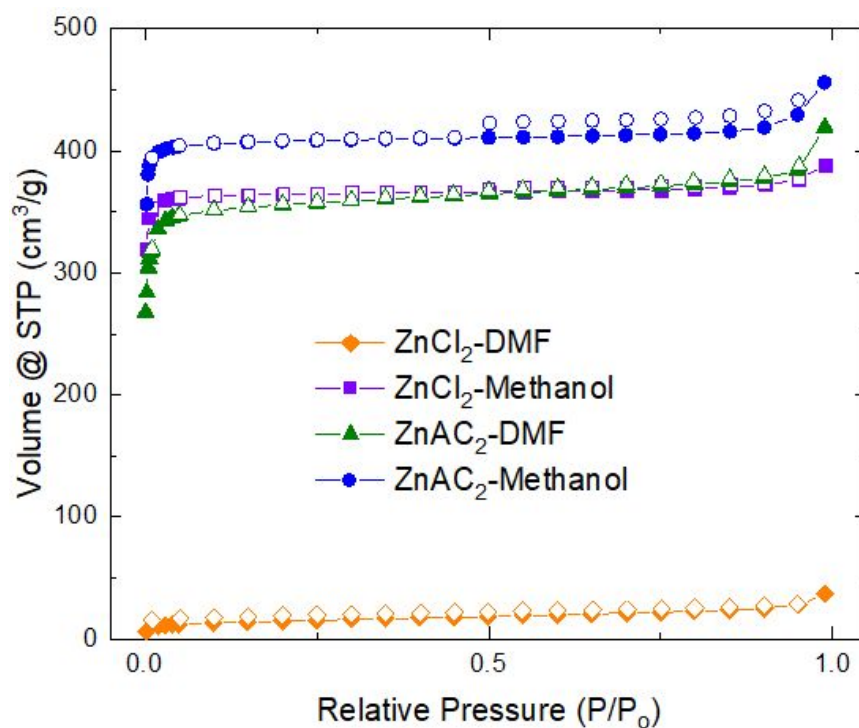


Figure S12: Nitrogen physisorption isotherms of $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ synthesized from different metal precursors ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) using methanol and DMF as solvents. Closed circles correspond to adsorption and open circles correspond to desorption.

References

- [1] Jasuja, H.; Burtch, N.; Huang, Y.; Cai, Y.; Walton, K. Kinetic Water Stability of an Isostructural Family of Zinc-Based Pillared Metal–Organic Frameworks. *Langmuir*. **2012**, 29, 633-642.
- [2] Jasuja, H.; Huang, Y.; Walton, K. Adjusting the Stability of Metal–Organic Frameworks under Humid Conditions by Ligand Functionalization. *Langmuir*. **2012**, 28, 16874-16880.
- [3] Chun, H.; Dybtsev, D.; Kim, H.; Kim, K. Synthesis, X-ray Crystal Structures, and Gas Sorption Properties of Pillared Square Grid Nets Based on Paddle-Wheel Motifs: Implications for Hydrogen Storage in Porous Materials. *Chem. Eur. J.* **2005**, 11, 3521-3529.
- [4] Chun, H.; Moon, J. Discovery, Synthesis, and Characterization of an Isomeric Coordination Polymer with Pillared Kagome Net Topology. *Inorg. Chem.* **2007**, 46, 4371-4373.
- [5] Zhou, K.; Chaemchuen, S.; Wu, Z.; Verpoort, F. Rapid Room Temperature Synthesis Forming Pillared Metal-Organic Frameworks with Kagome Net Topology. *Microporous Mesoporous Mater.* **2017**, 239, 28-33.
- [6] University of California Berkley Department of Chemistry.
<http://www.cchem.berkeley.edu/rsgp/solventproperties.pdf>. (Accessed 8/2/2018)
- [7] Sigma-Aldrich.
<https://www.sigmaaldrich.com/catalog/product/aldrich/186317?lang=en®ion=US>.
(Accessed 8/2/2018)
- [8] R. Stenutz. <http://www.stenutz.eu/chem/solv6.php?name=N,N-diethylformamide>.
(Accessed 8/2/2018)
- [9] Liang, Z.; Marshall, M.; Chaffee, A. CO₂ Adsorption, Selectivity and Water Tolerance of Pillared-layer Metal-Organic Frameworks. *Microporous Mesoporous Mater.* **2010**, 132, 305-310.
- [10] Tan, K.; Nijem, N.; Canepa, P.; Gong, Q.; Li, J.; Thonhauser, T.; Chabal, Y. Stability and Hydrolyzation of Metal Organic Frameworks with Paddle-Wheel SBUs upon Hydration. *Chem. Mater.* **2012**, 24, 3153-3167.
- [11] Lee, J.; Olson, D.; Pan, L.; Emge, T.; Li, J. Microporous Metal-Organic Frameworks with High Gas Sorption and Separation Capacity. *Adv. Funct. Mater.* **2007**, 17, 1255-1262.