Understanding the Stability of Metal-Organic Frameworks under Humid Conditions

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School of Chemical & Biomolecular Engineering

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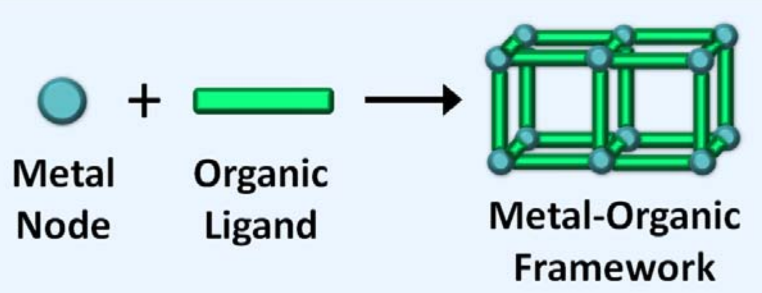
Metal-Organic Frameworks (MOFs)

Structural Properties



Structural diversity: >20,000 structures

- Surface area: ~ 400 - 7000 m^2/g
- Pore volume: ~ 0.2 – 4.0 m/g
- Pore sizes: ~ 0.3 – 3.0 nm

Promising applications

Drug delivery[1]

Heterogeneous catalysis[2]

Chemical sensing[3]

Air purification[4]

Clean energy storage[5]

1. Horcajada et al. *J. Amer. Chem. Soc.* 2008 130, 6774.
2. Lee et al. *Chem. Soc. Rev.* 2009 38, 1450.
3. Kreno et al. *Chem. Rev.* 2012 112, 1105.
4. DeCoste et al. *Chem. Rev.* 2014 114, 5695.
5. Li et al. *Chem. Comm.* 2010 46, 44.

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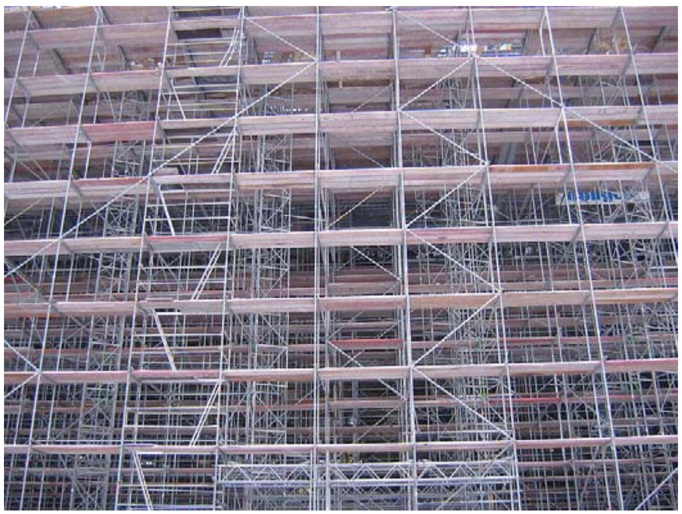
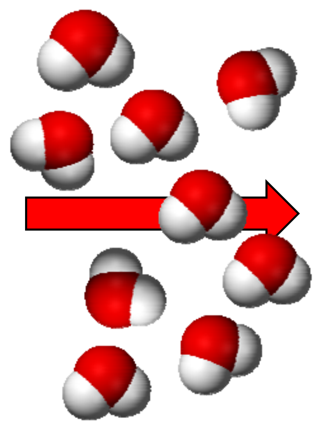
Designer Materials: Optimize Selectivity, Capacity, Functionality... But

Is it stable?

- Why? Why not? Can it be fixed?





Challenges in Understanding Water Stability

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- Not large number of MOF families that can be systematically varied to control for certain features
- Variety of MOFs is high – how to generalize results?
- Water stable vs water repellent
- Cyclic stability and aging effects
- Water vapor exposure vs. liquid water
- Relative to other gases/vapors, water adsorption in MOFs has not been widely investigated

MOF Stability: Introduction

- First water isotherm reported by Bülow and coworkers[1] in 2002 (HKUST-1/Cu-BTC)
- Kaskel and coworkers[2] did more in-depth analysis of water adsorption in HKUST-1 in 2009
- From 2002-2012, only 2-3 studies per year reported water adsorption in MOFs

1. Wang, Q. M. et al. Microporous Mesoporous Mater. 2002, 55, 217.
2. Kusgens, P. et al. Microporous Mesoporous Mater. 2009, 120, 325.

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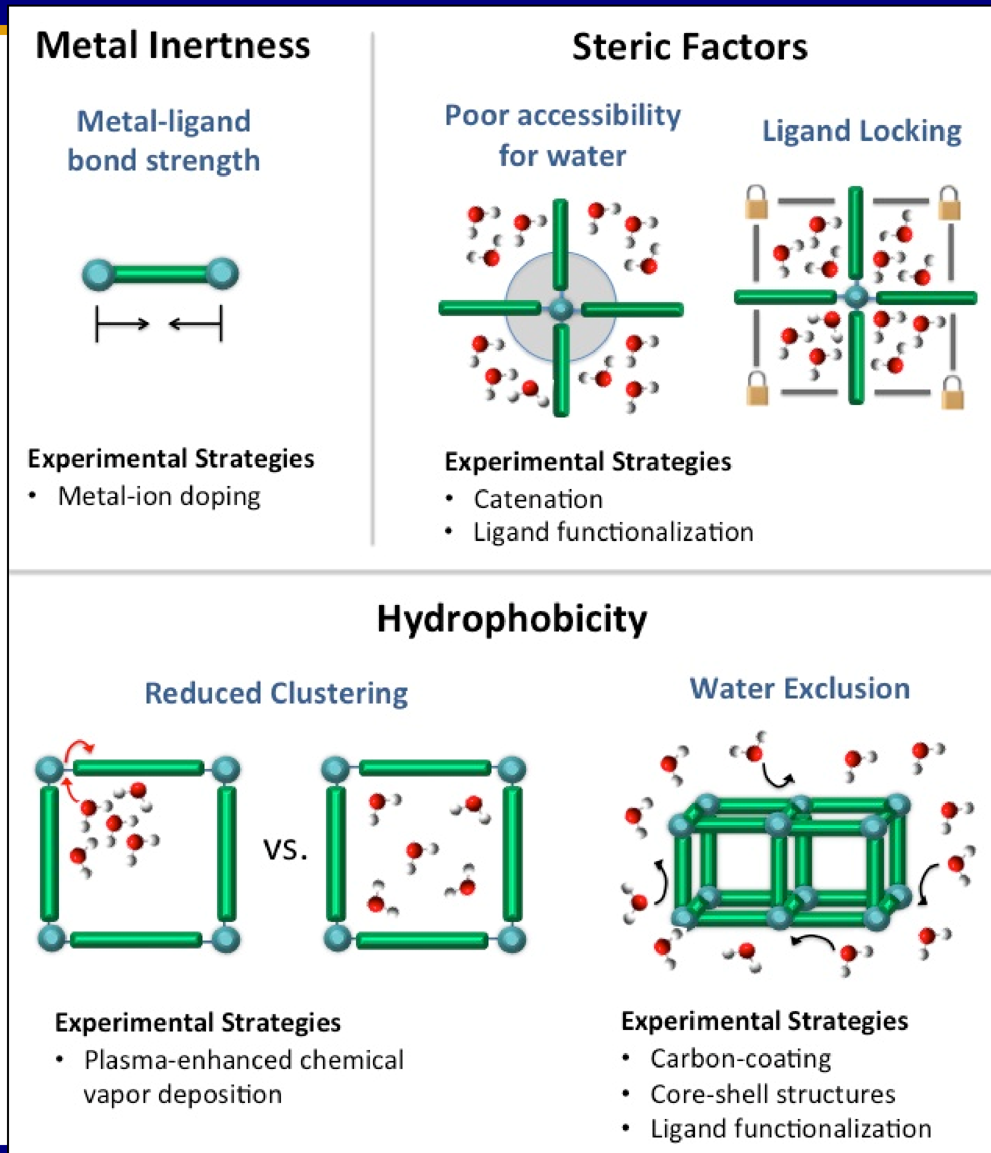
MOF Stability: Introduction

- Since 2012, several features began to emerge as being important contributors to stability:
  - Basicity of the ligand
  - Extent of coordination (metal-ligand bond character)
  - Sterics introduced by ligand functionalization



Burtch, N. C., H. Jasuja, K. S. Walton, *Chemical Reviews*, 2014, 114, 10575-10612.

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Defining Water Stability

- Is it stable?
  - Generally means: can the material be exposed to humidity or does it require special handling
- PXRD and BET analysis before and after water exposure
  - Water introduced to sample with carrier gas or to vacuum (instrument dependent)
- Immerse in liquid water
  - MOFs can be stable to vapor but not to aqueous conditions
  - More stringent test

Today's Presentation

- Materials Focus:
  - UiO-66 and MIL-53(Al)
  - Zn-BDC-DABCO (Zn-DMOF)
- Methods:
  - Water vapor adsorption studies
  - NMR, FTIR, molecular modeling
- Classifying water stability

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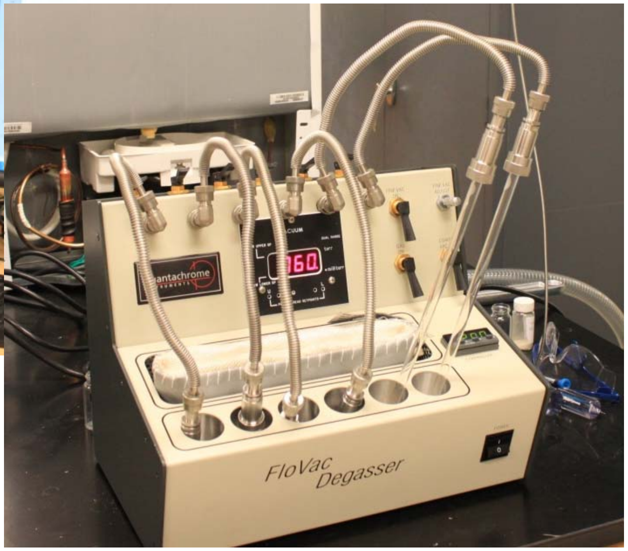
BET Analysis

Quadrasorb from Quantachrome



- Four sample stations with dedicated P0 measurement at each station
- Independent adsorption measurements
- Krypton option for micropore characterization

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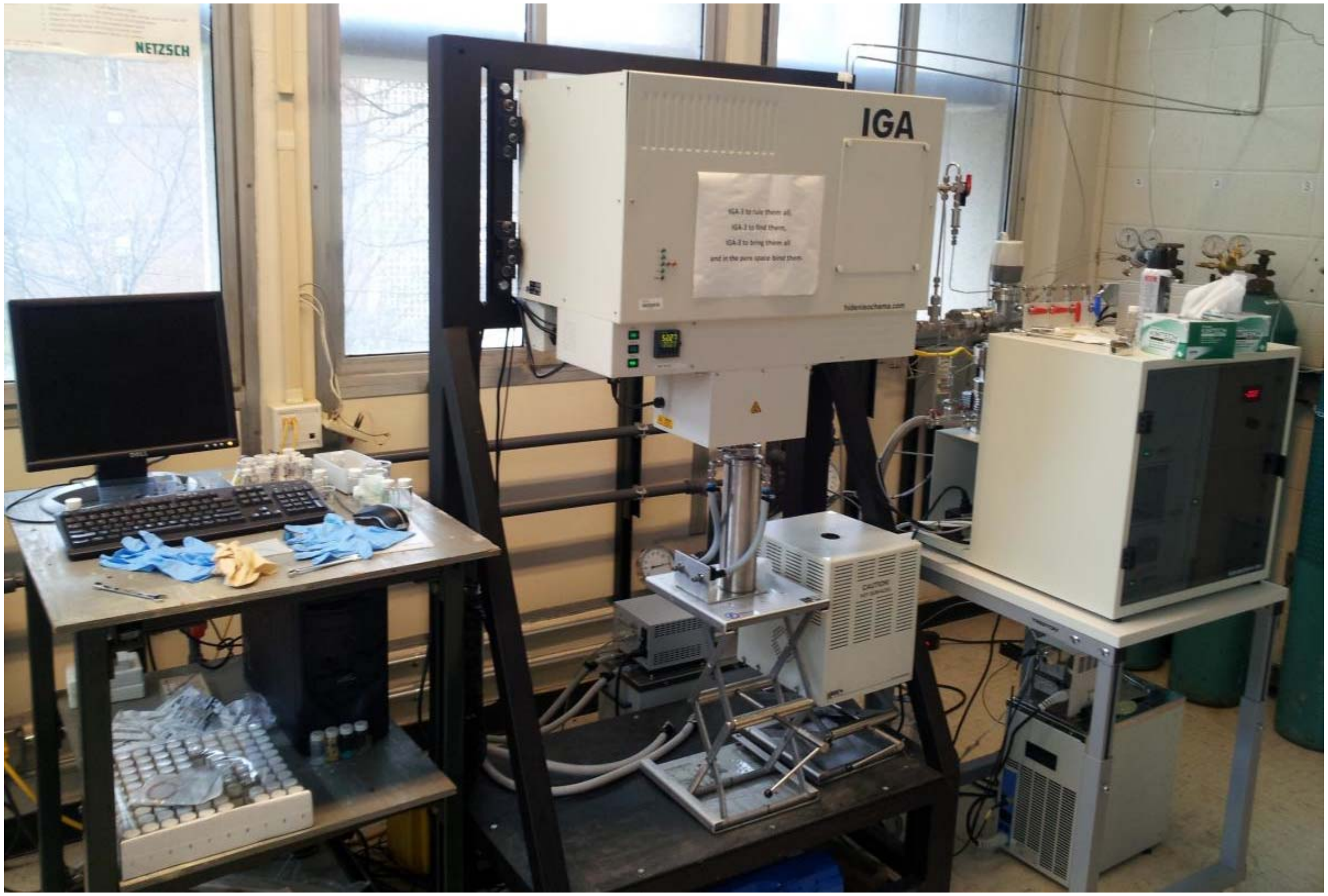
Water Vapor Measurements
Hiden Isochema IGA-3

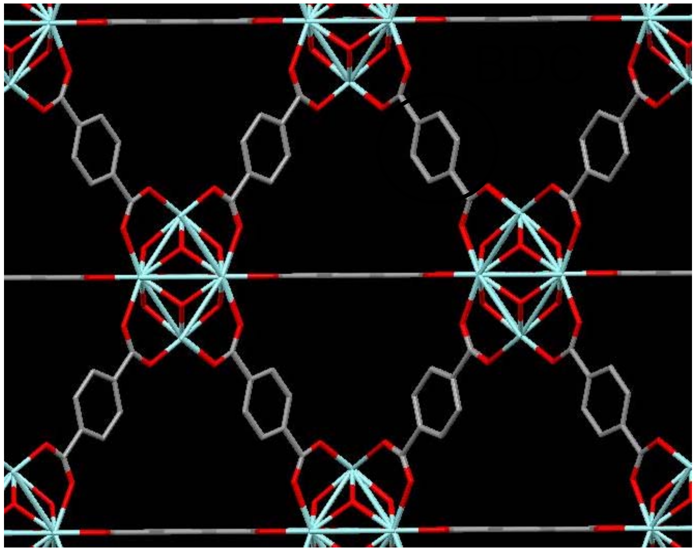


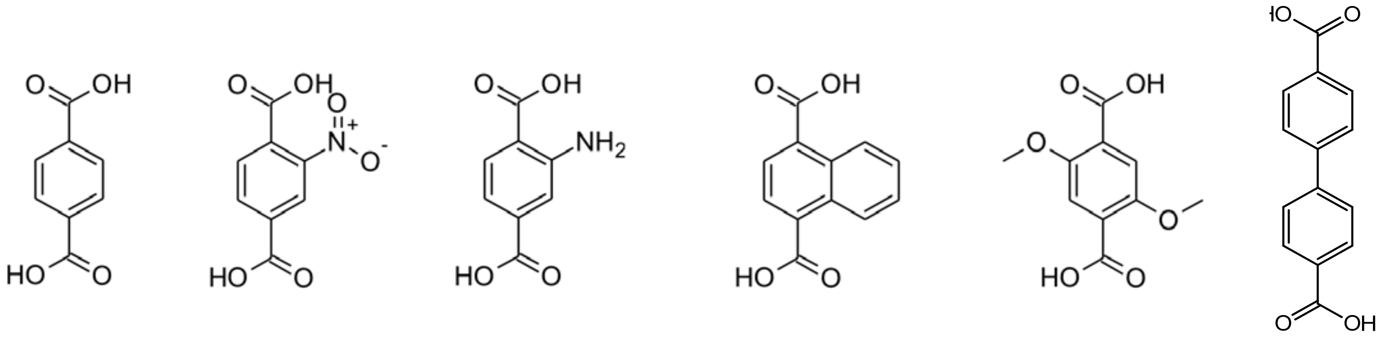
- Air is bubbled through reservoir of water and the instrument controls humidity level
- 0 bar – 20 bar
- -196° C – 1000° C

UiO-66: Maintain Topology but Change Ligand

UiO-66-X/UiO-67

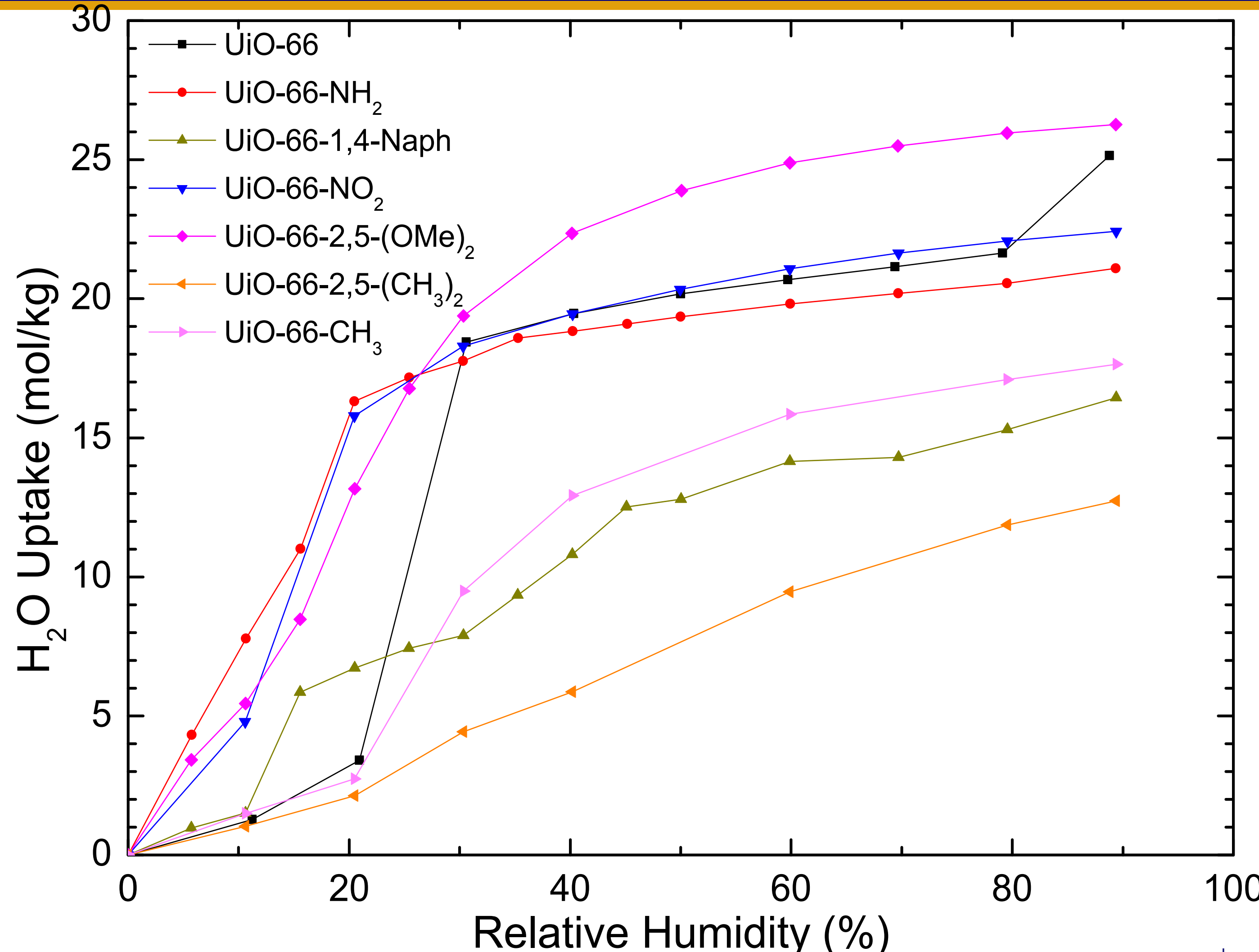
- We know Zr-BDC (UiO-66) is very stable [1]
- How does functionalization impact stability?
- Some disagreement on effect of ligand length





1. Lillerud et al, 2008, *130*, 13850–13851

Water Adsorption in UiO-66-X at 298 K



Cmarik, G., Kim, M.; Cohen, S.M. and Walton, K.S., *Langmuir*, 2012, 28(44), 15606-15613.

UiO-66: Maintain Topology but Change Ligand

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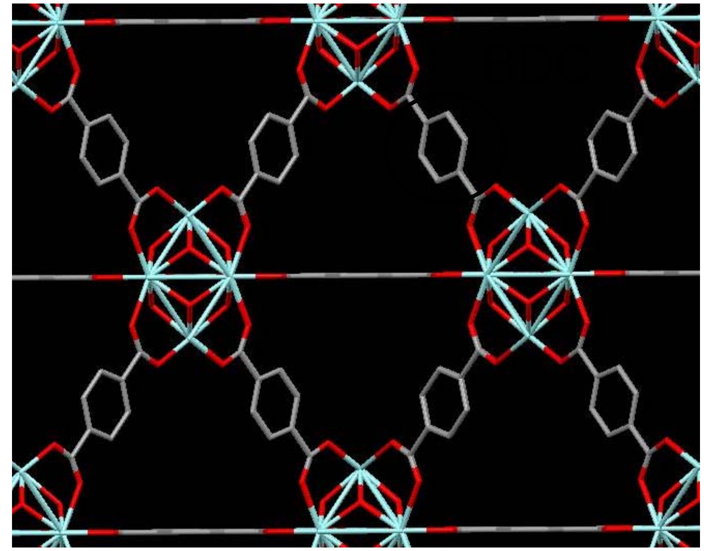
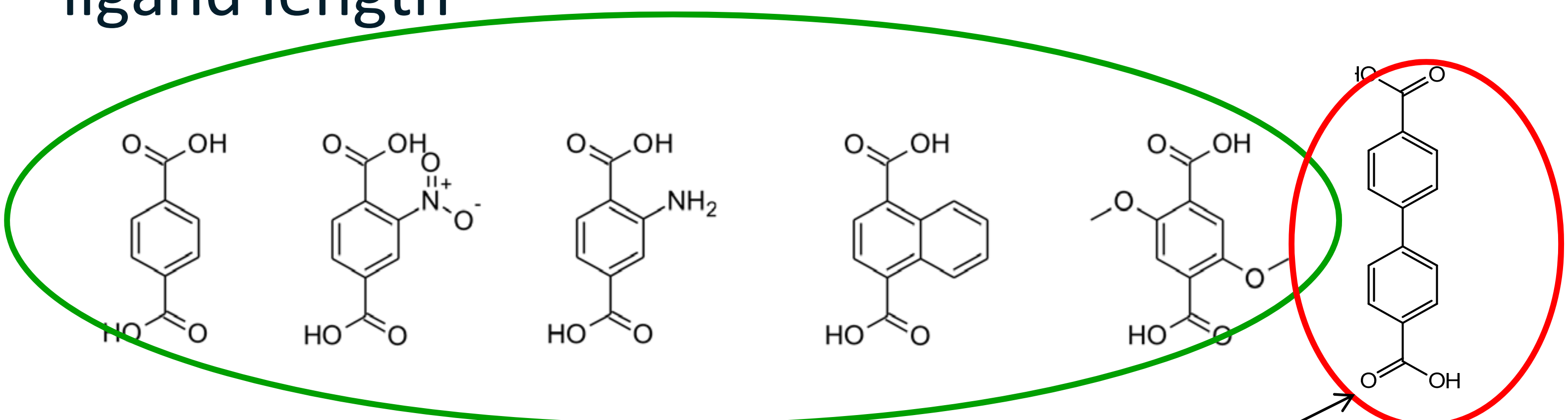
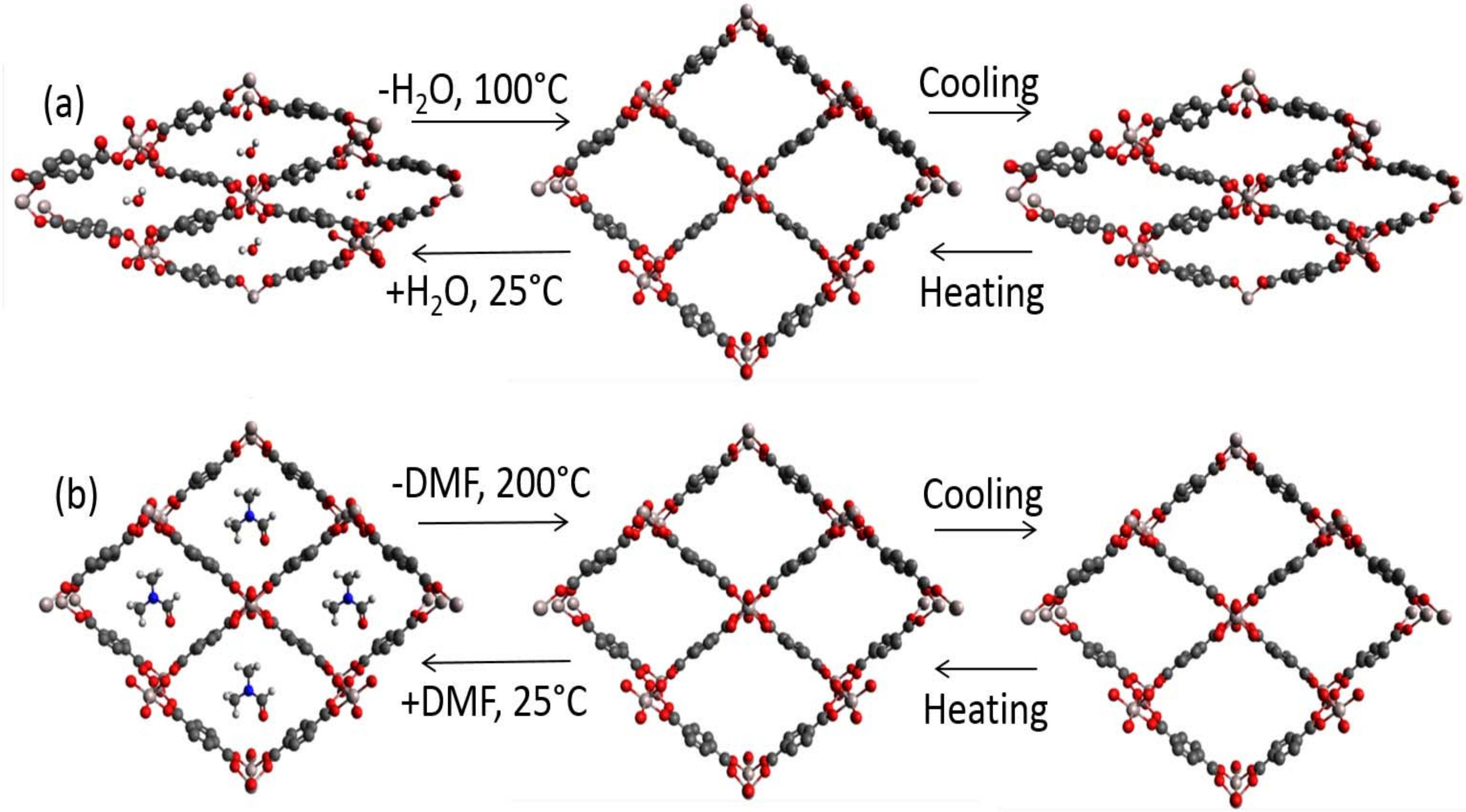




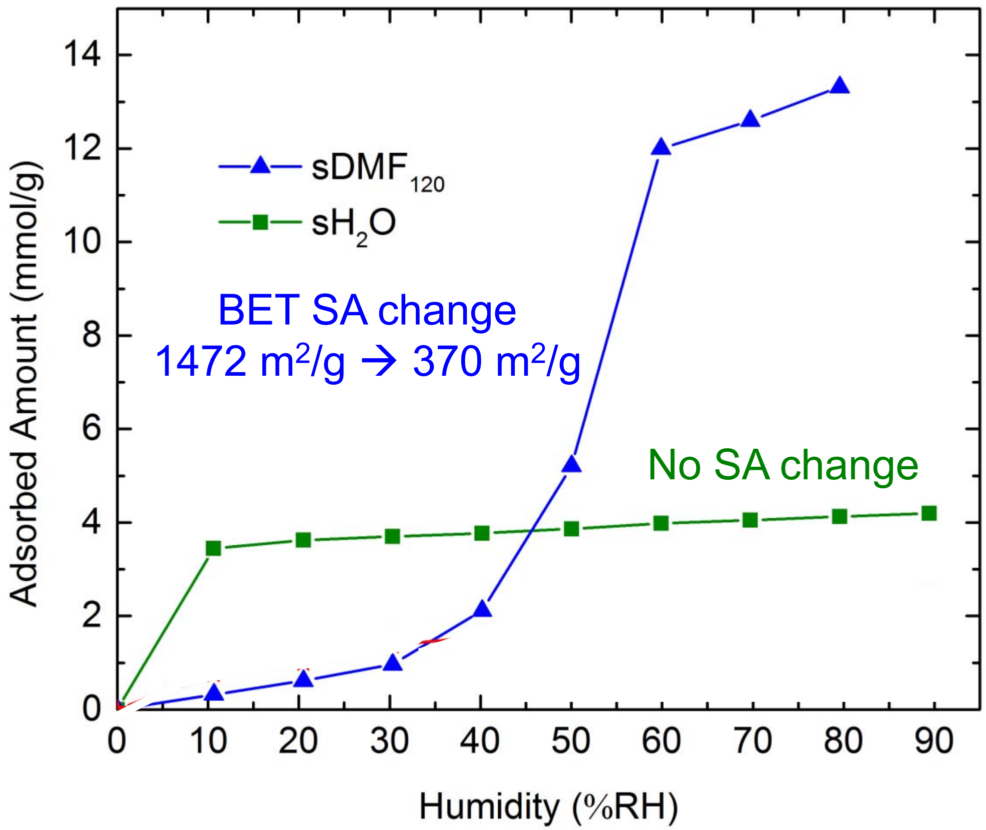
Mondloch, JE, et al. ChemComm. 2014;50(64):8944-8946
DeCoste JB, et al. J. of Mat. Chem A, **2013**, 1, 5642-5650

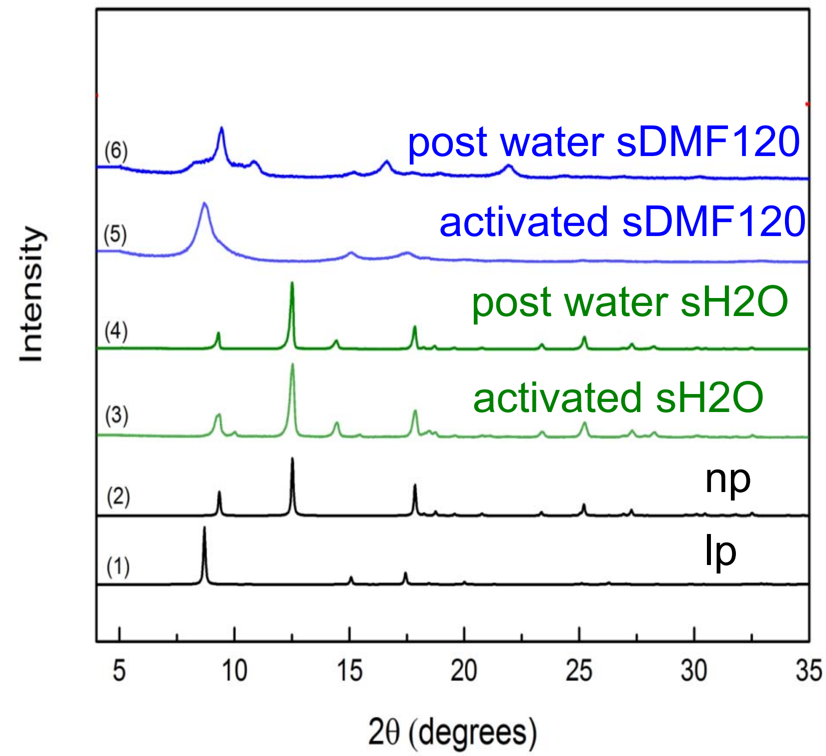
Breathing Behavior of MIL-53(Al)



W. Mounfield, K. S. Walton, submitted.
Loiseau, T. et al.. *Chem-Eur J* **2004,** *10*, 1373

Water Vapor Adsorption in MIL-53(Al), 298 K

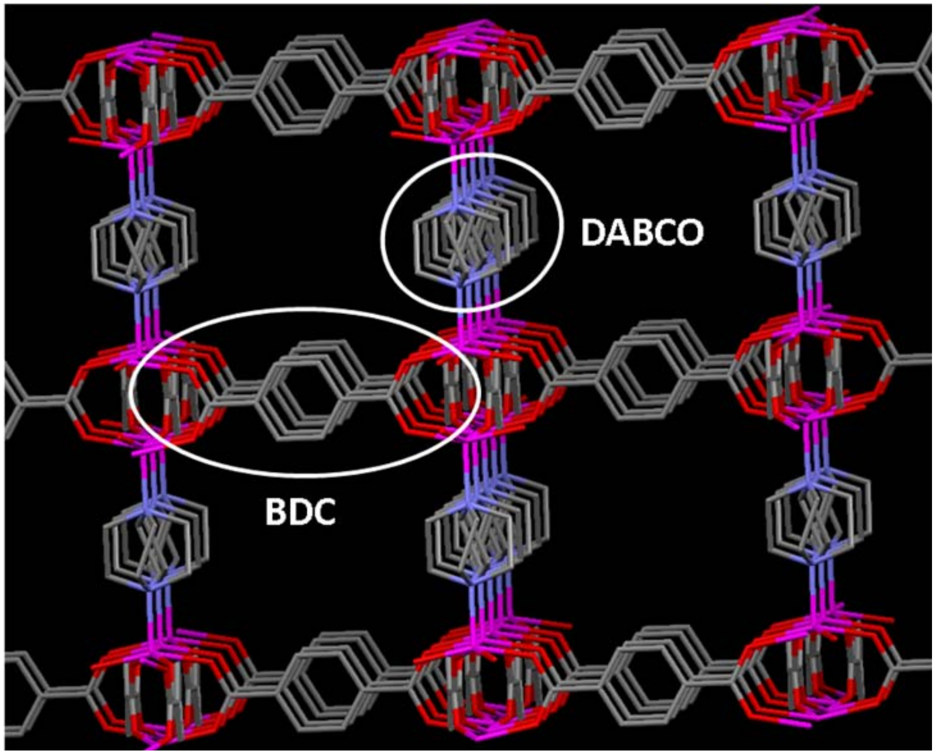




W. Mounfield, K. S. Walton, submitted.

Zn-BDC-DABCO or “DMOF”

N-coordinated zinc from DABCO



DMOF is stable up to 40% RH

DMOF-NH_2 degrades at water exposure well below 40%RH

Dybtsev et al., *Angew. Chem.-Int. Edit.*, 43, 2004.
Schoenecker, Walton, et al., *IECR*, 51 (18), 6513–6519.

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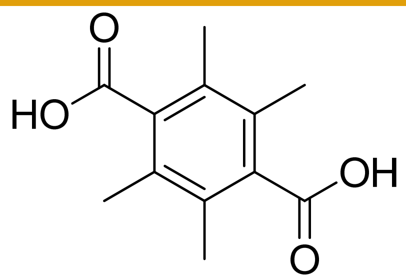
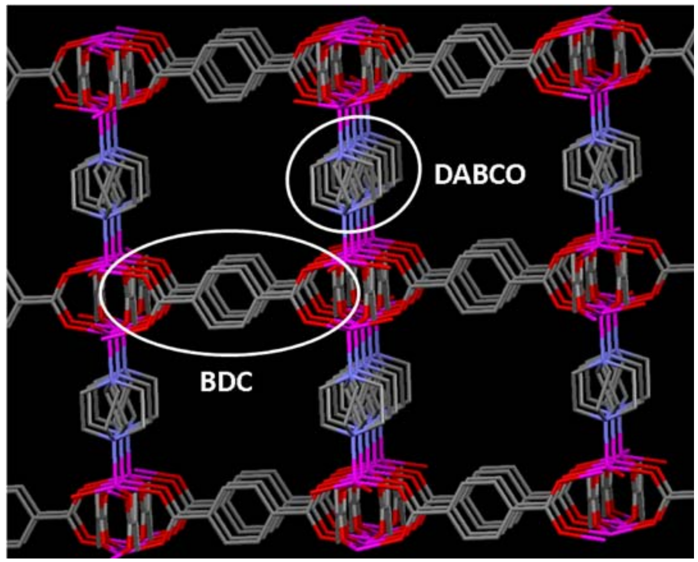
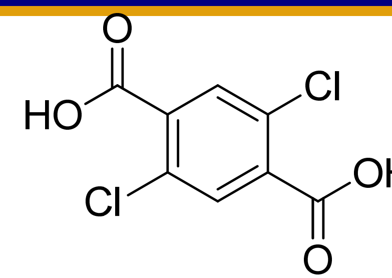
Impact of Functional Groups on Zn-DMOF Stability

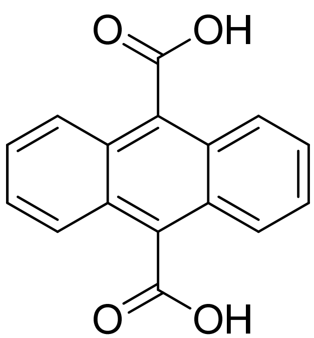


TMBDC
tetramethyl-1,4-benzenedicarboxylate

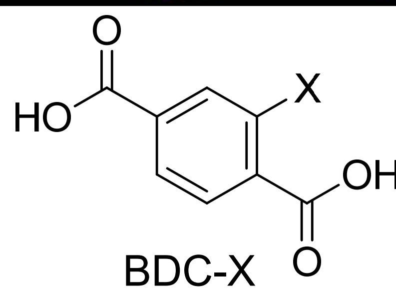




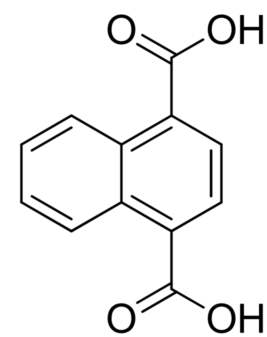
BDC-Cl_2
2,5-dichloro-1,4-benzenedicarboxylate



ADC
anthracenedicarboxylate



BDC-X
2-X 1,4-benzene dicarboxylate
X =
nitro (-NO_2)
hydroxy (-OH)
bromo (-Br)



NDC
1,4-naphthalenedicarboxylate

Jasuja, H., K. S. Walton, et al. *Langmuir*, 2012, 28(49), 16874-16880.

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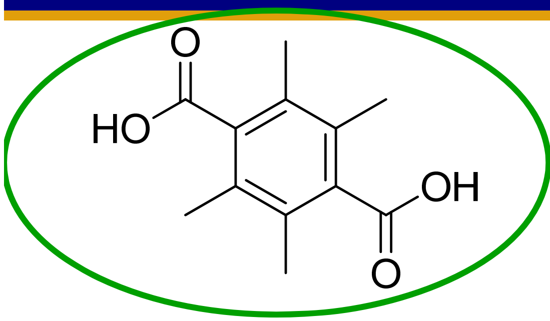
Impact of Functional Groups on Zn-DMOF Stability



TMBDC
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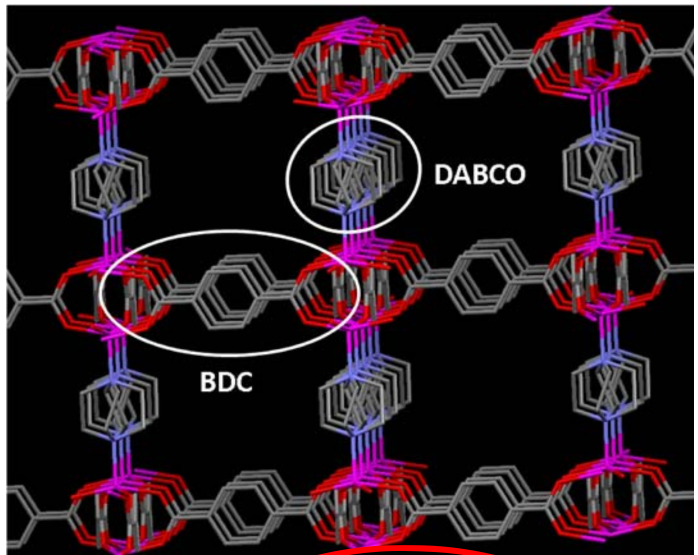

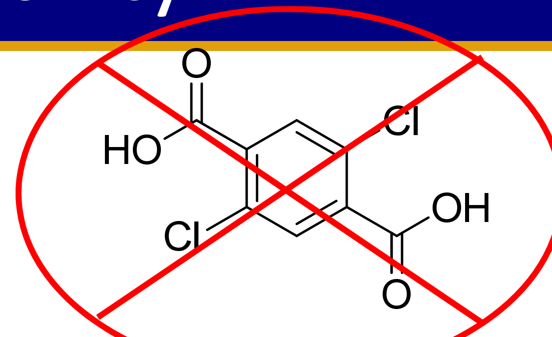

$BDC-Cl_2$
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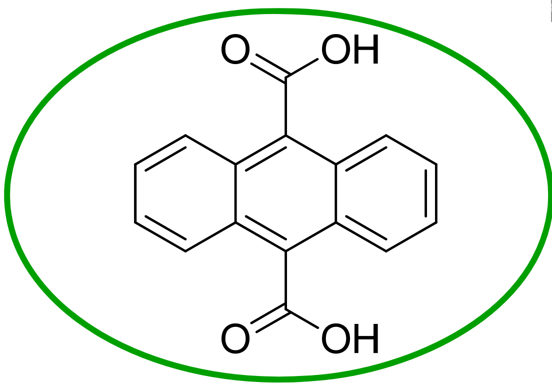

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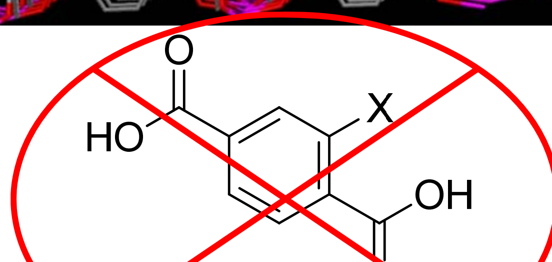

BDC-X
2-X 1,4-benzene dicarboxylate
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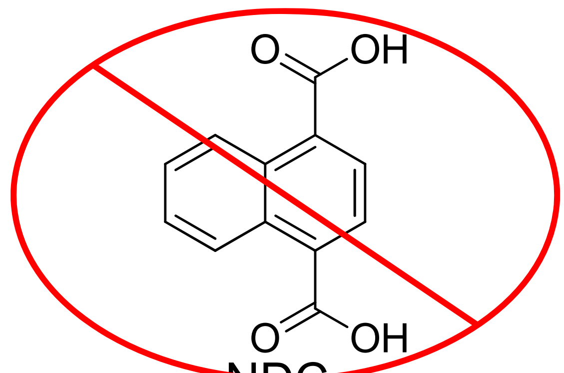

NDC
1,4-naphthalenedicarboxylate

Jasuja, H., K. S. Walton, et al. *Langmuir*, 2012, 28(49), 16874-16880.

Zn-DMOF-Br PXRD Before/After Water Exposure

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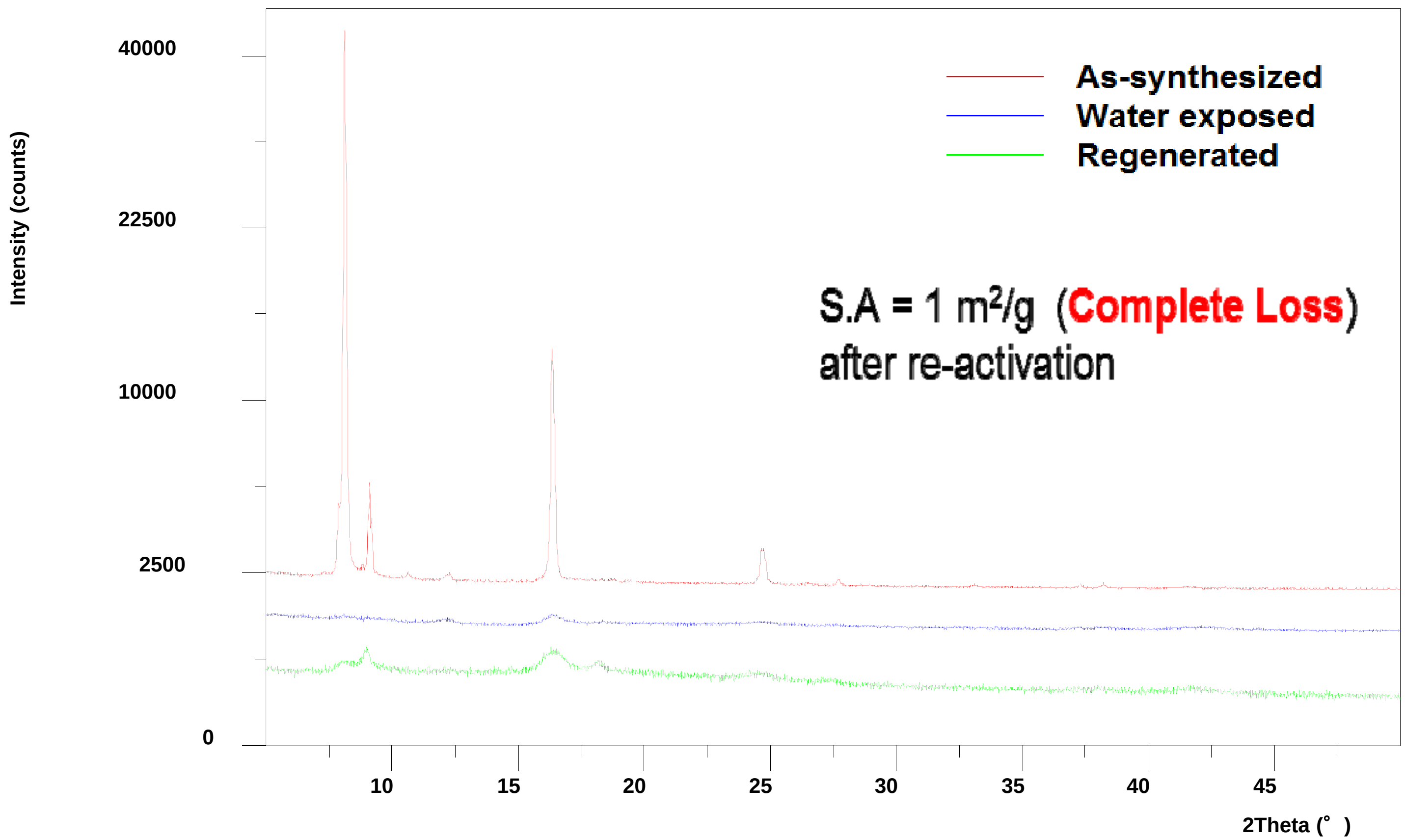

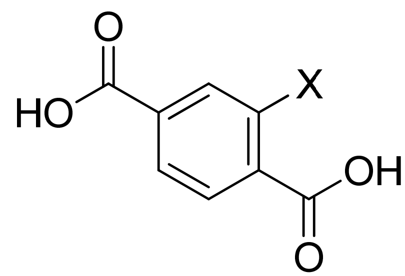

Jasuja, H., K. S. Walton, et al. *Langmuir*, 2012, 28(49), 16874-16880.

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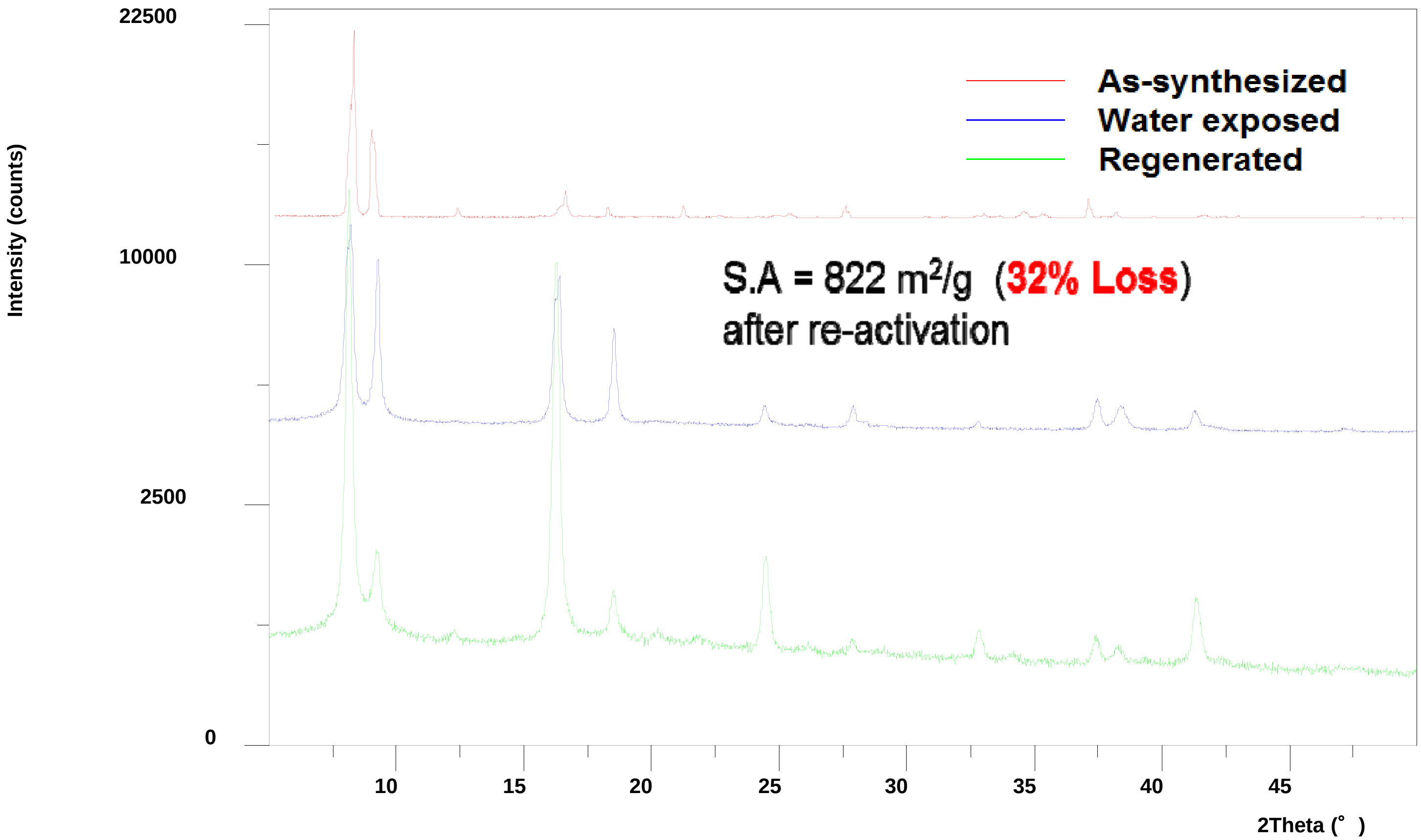
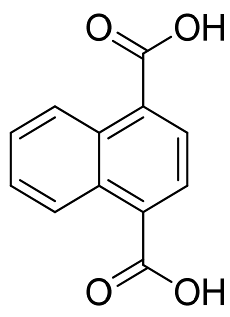
Zn-DMOF-N PXRD Before/After Water Exposure

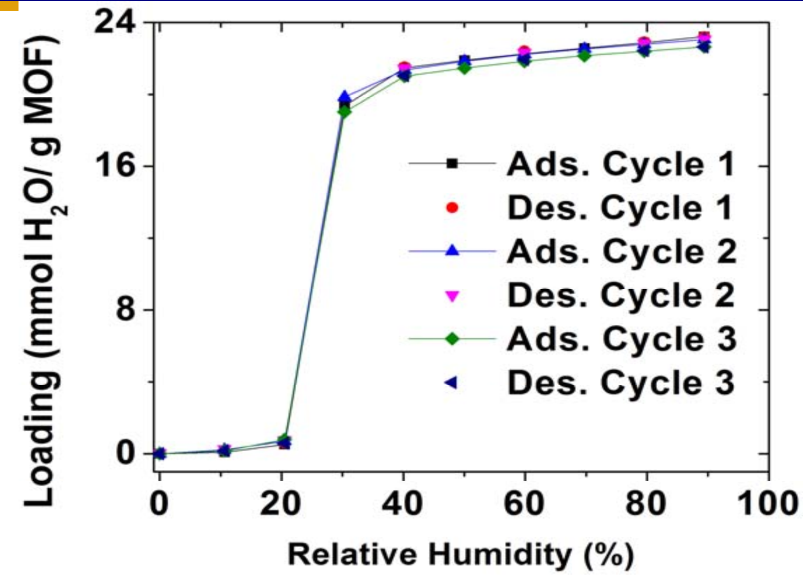


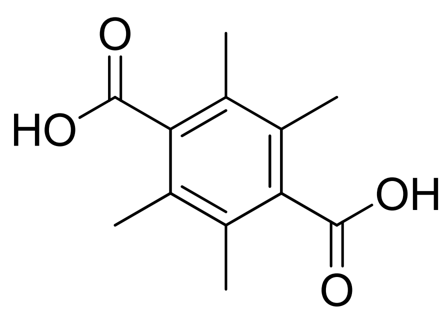


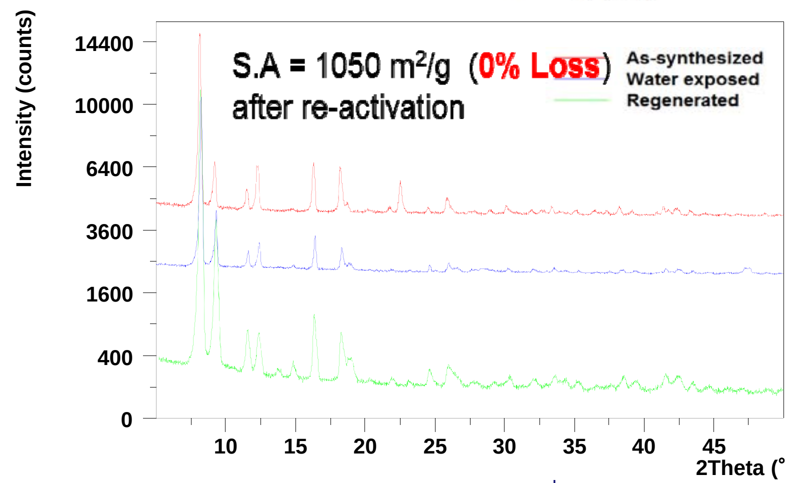
Jasuja, H., K. S. Walton, et al. *Langmuir*, 2012, 28(49), 16874-16880.

DMOF-TM2 Maintains Crystallinity and Surface Area

- After 3 cycles of adsorption/desorption of water vapor up to 90% RH
- Sample left in lab air for ~ 2 years
  – unchanged SA/PXRD

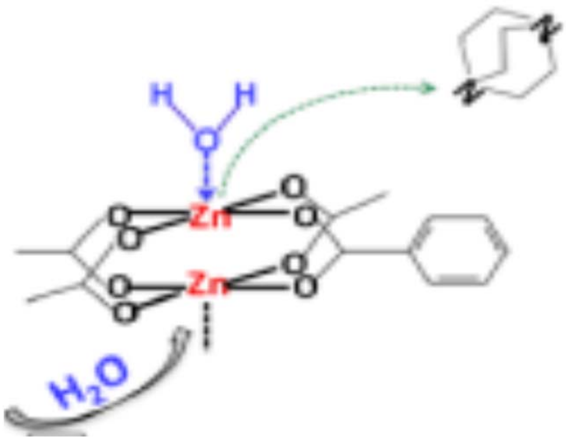




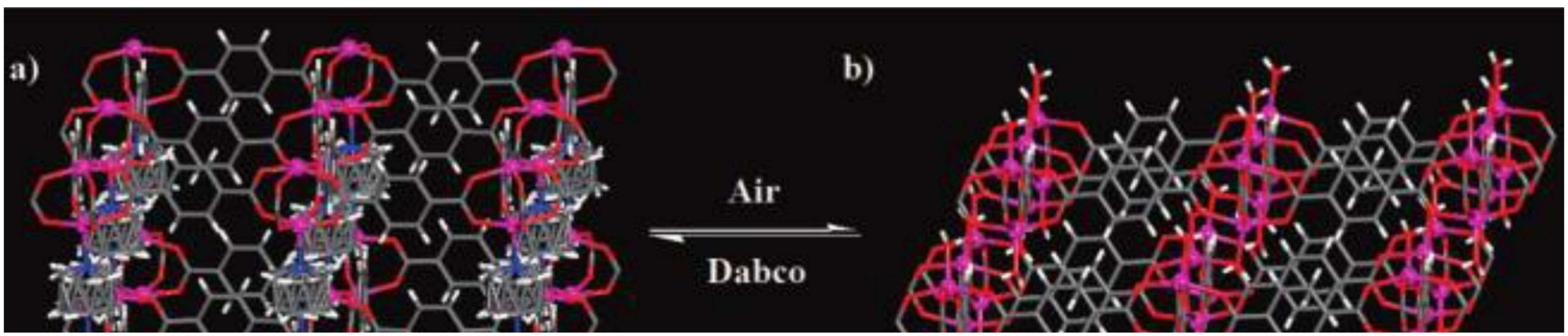


Jasuja, H., N. C. Burtch, Y.-G. Huang, Y. Cai, K. S. Walton., *Langmuir,* 2013, *29*, 633.

Is BDC or DABCO the Culprit?



- Studies have shown that DABCO leaves first when attacked by water
- The Zn-BDC layers remain
- The MOF reassembles when placed in DMF



Tan, K. et al., *Chemistry of Materials* 2012, 24.
Chen, Z. et al, *Crystal Growth & Design* 2009, 9.

Thermodynamic Stability

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Burtch, N. C., H. Jasuja, K. S. Walton, Water Stability and Adsorption in Metal-Organic Frameworks, *Chemical Reviews*, 2014, 114, 10575-10612.

Stability Mechanism	Governing Structural Factors
Unfavorable for irreversible hydrolysis reaction to occur under *any* water loading	**Inertness of Metal Cluster** **Metal-Ligand Bond Strength** Ligand effects •pKa of coordinating atom Metal effects •oxidation state •ionic radius **Lability with Water** Metal species •Reduction potential •Irving-Williams sequence •LUMO energetics Coordination geometry •Pauling rules

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Kinetic Stability

Burtch, N. C., H. Jasuja, K. S. Walton, Water Stability and Adsorption in Metal-Organic Frameworks, *Chemical Reviews*, 2014, 114, 10575-10612.

Water *could* hydrolyze the bond, but…

Not favorable because water molecules cannot cluster near metal site

Hydrophobicity

Water unable to adsorb in pores

- Pore hydrophobicity

Water unable to cluster near metal

- Internal hydrophobicity

Water is able to approach metal sites, yet not favorable because of transition state energetics

Steric Factors

Around Metal Sites

Related to ease of water approach

- Coordination # of metal
- Structural transitions

Around Labile Ligands

Related to ease of displacing ligand

- ligand 'packing' in structure
  - Interpenetration
  - Bulky functional groups

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Classifying Water Stability

Burtch, N. C., H. Jasuja, K. S. Walton, Water Stability and Adsorption in Metal-Organic Frameworks, *Chemical Reviews*, 2014, 114, 10575-10612.

Criteria for Water Stability Classification	
thermodynamically stable	stable after long-term exposure to aqueous solutions: week or greater in pure water, day(s) in acidic/basic or boiling conditions *strong potential for a wide range of applications*
high kinetic stability	stable after exposure to high humidity conditions: decomposes after short exposure times in liquid water *strong potential for industrial applications with high humidity conditions*
low kinetic stability	stable under low humidity conditions *potential for applications with predried gas conditions*
unstable	quickly breaks down after any moisture exposure *potential for applications under moisture-free conditions*

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Testing Conditions and Guidelines

Burtch, N. C., H. Jasuja, K. S. Walton, Water Stability and Adsorption in Metal-Organic Frameworks, *Chemical Reviews*, 2014, 114, 10575-10612.

	APPLICATION	TESTING CONDITIONS	POST-CHARACTERIZATION
Gas or Vapor Phase			
One-Time Use	Single-Pass cartridge	Prolonged stability in ambient air	PXRD and BET
Multiple Use	Industrial Separations	Cyclic exposure to relevant mixture; regeneration via P or T swing	PXRD and BET; change in working capacity
	Gas Storage	Prolonged stability under relevant storage conditions	PXRD and BET
	Membrane or Thin films	Prolonged stability under application conditions	PXRD and BET; SEM, TEM, or other surface analysis
Aqueous Phase	Catalysis, liquid separations, trace metals	Immersion and stirring under aqueous conditions	PXRD, BET, solid phase mass loss after sample filtration

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