An Entirely New Molecular Glue Using Unusual Structural Transformation of a Coordination Polymer

Korea Science Academy

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1 Introduction

2 Synthesis

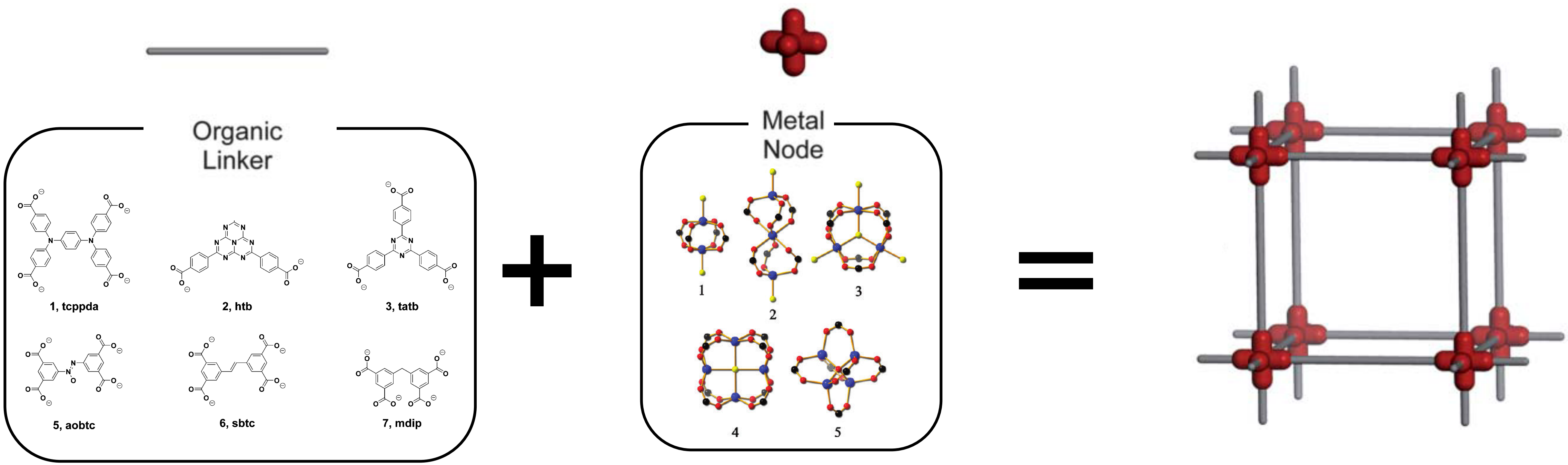
3 Result & Discussion

4 Conclusion

Introduction

MOF

Metal-Organic Framework



- More than 20,000 different types
- Permanent Porosity and Great Surface Area
- Many potential applications (gas storage, separation, material recognition, drug delivery and catalyst)

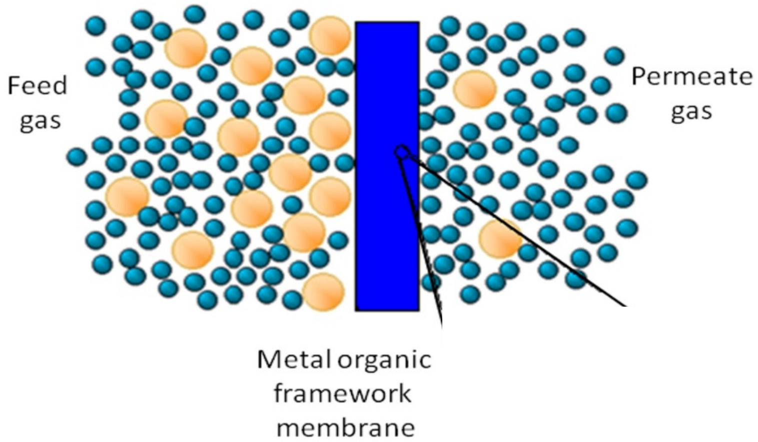
CrystEngComm, 2012, 14, 3839–3846
ACCOUNTS OF CHEMICAL RESEARCH Vol. 44, No. 2 ’ 2011 ’ 123–133

MOF Application

1. Fuel Cell / Hydrogen Storage

2. Carbon Dioxide Capture and Storage

3. Gas Separation & Filtration

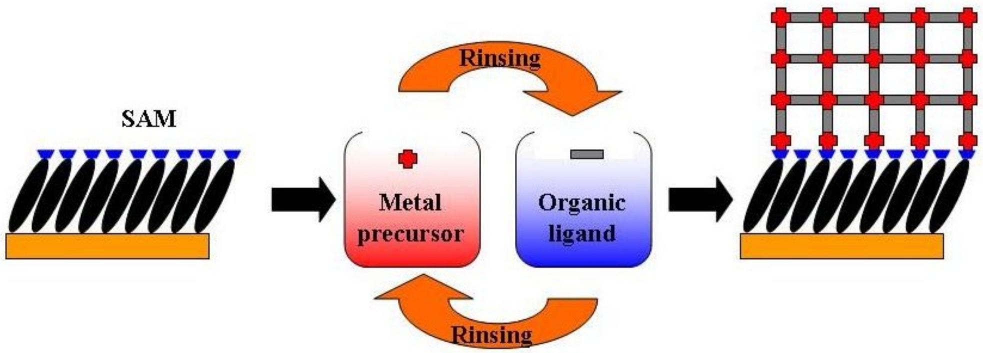


MOF Film

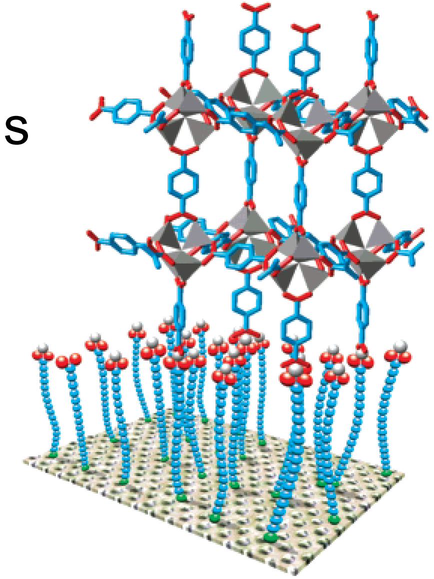
- Easy Operation & Control
- Effective Gas Separation
- High Thermal Stability
- Functionalized Pore

Fabrication of MOF Films

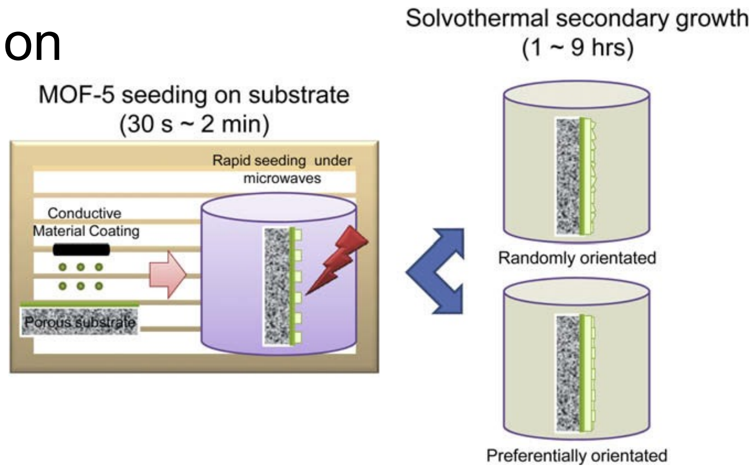
1. Layer-by-layer growth



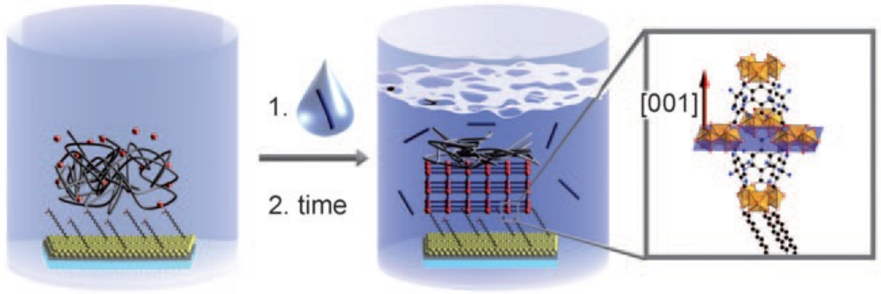
2. Growth/deposition from solvothermal mother solutions



3. Microwave-induced t
hermal deposition



4. Gel-layer synthesis

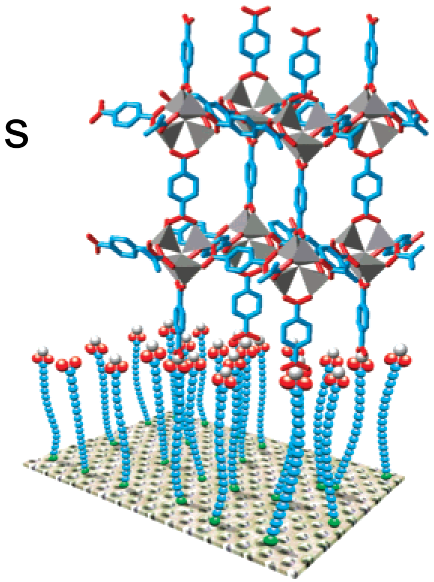


Materials 2010, 3, 1302-1315
J. AM. CHEM. SOC. 2005, 127, 13744-13745
Microporous and Mesoporous Materials 123 (2009) 100–106
Angew. Chem. Int. Ed. 2010, 49, 7225 –7228

Fabrication of MOF Films

1. Layer-by-layer growth

2. Growth/deposition from solvothermal mother solutions

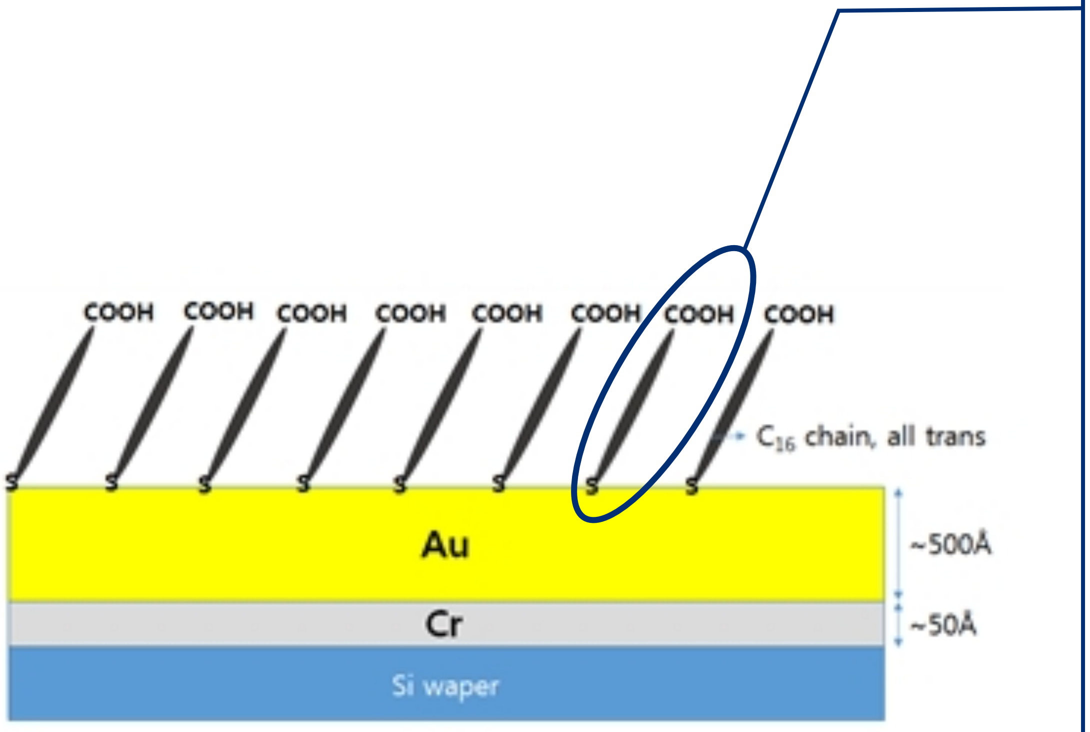


3. Microwave-induced thermal deposition

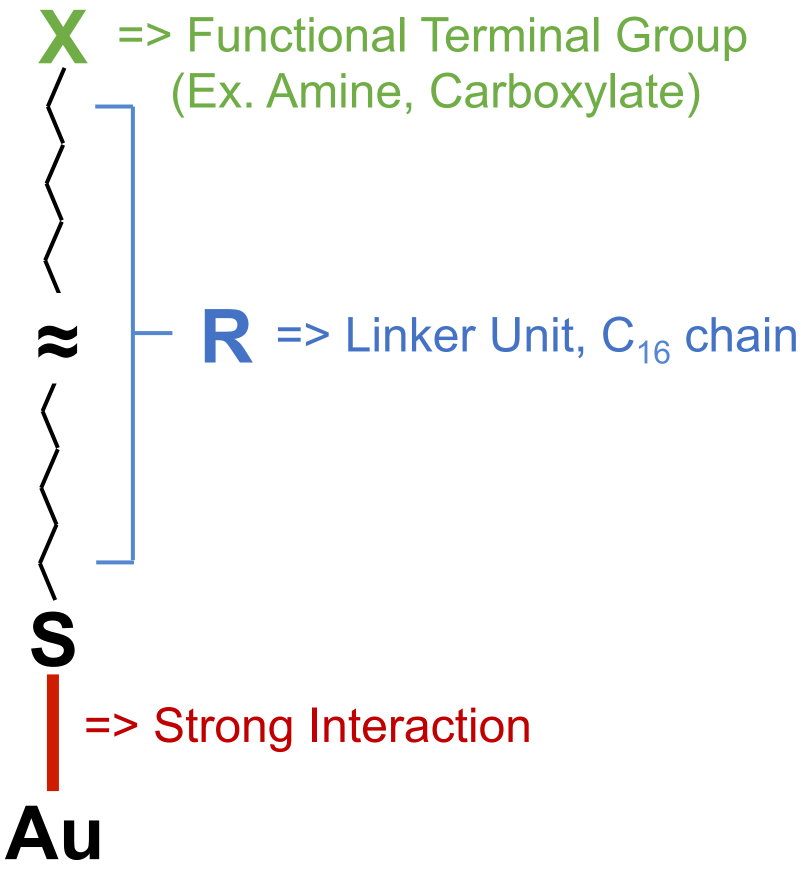
4. Gel-layer synthesis

Materials 2010, 3, 1302-1315
J. AM. CHEM. SOC. 2005, 127, 13744-13745
Microporous and Mesoporous Materials 123 (2009) 100–106
Angew. Chem. Int. Ed. 2010, 49, 7225 –7228

Self-Assembled Monolayer



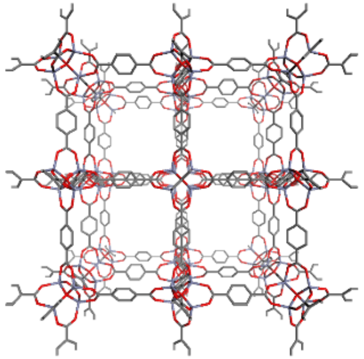
< Carboxylate-terminated Au Chip >

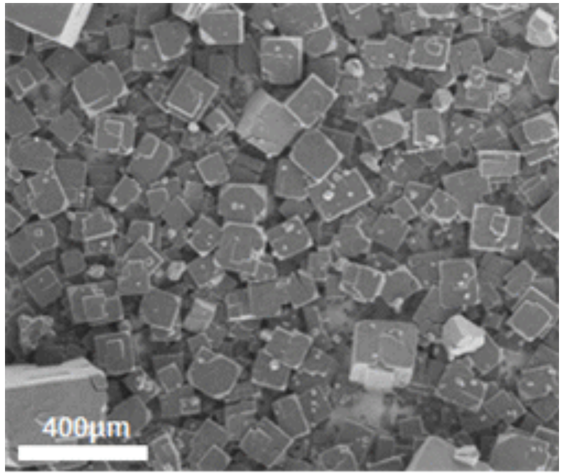


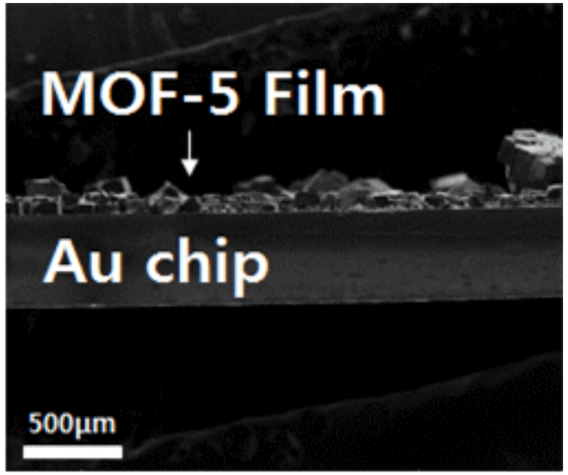
< X-terminated Au Chip >

MOF-5

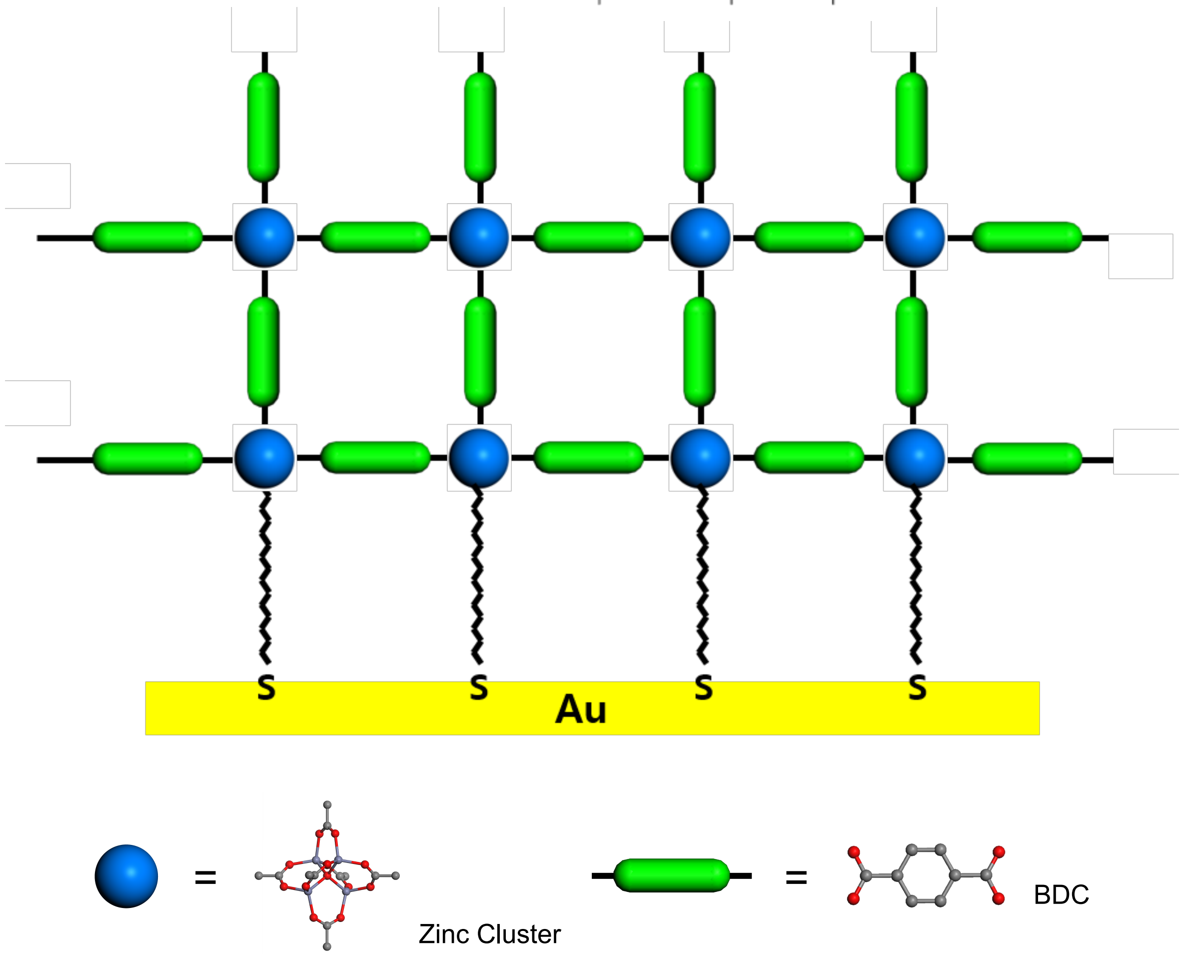
+ COOH Terminated Au Chip



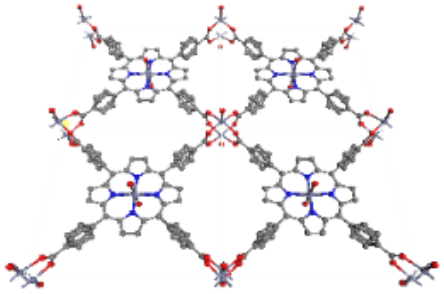




Diagram

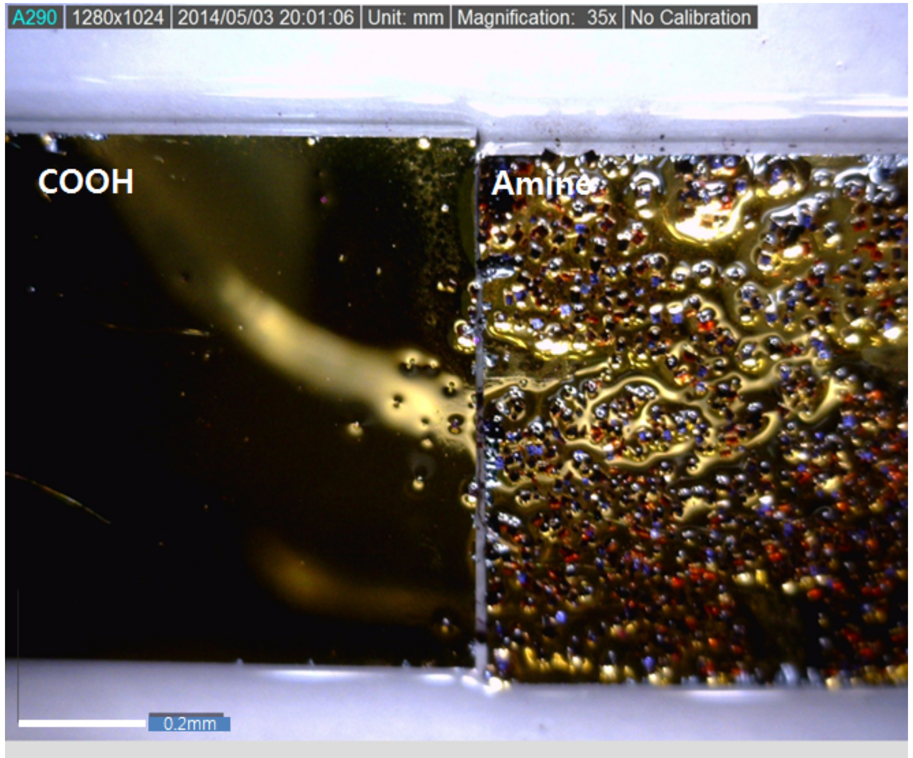


PPF-1



(Porphyrin Paddlewheel Framework)

COOH
Terminated
Au Chip

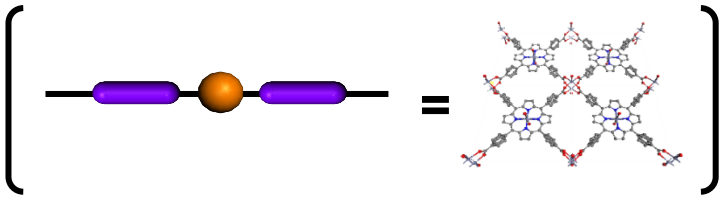


NH_2
Terminated
Au Chip

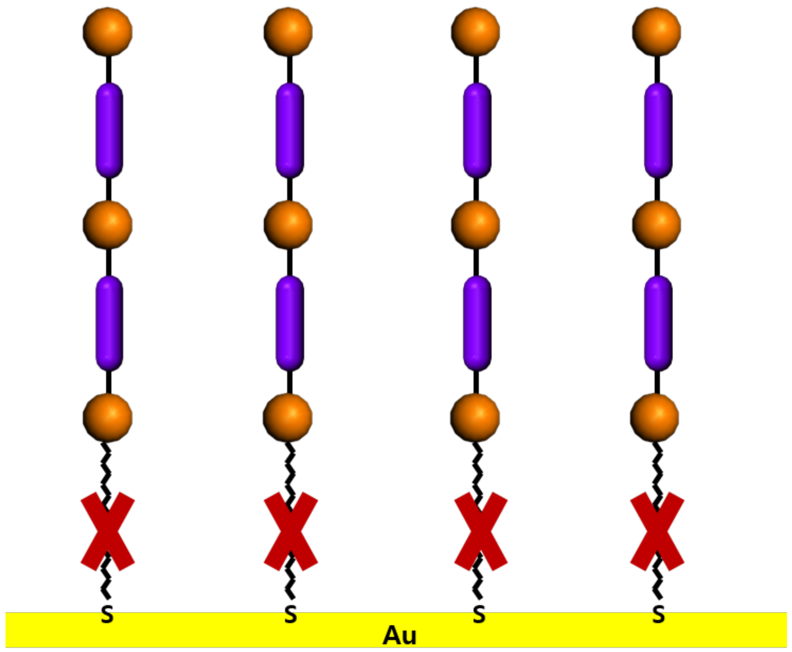
Weak interaction between PPF-1 and Au chip

Strong interaction between PPF-1 and Au Chip

PPF-1

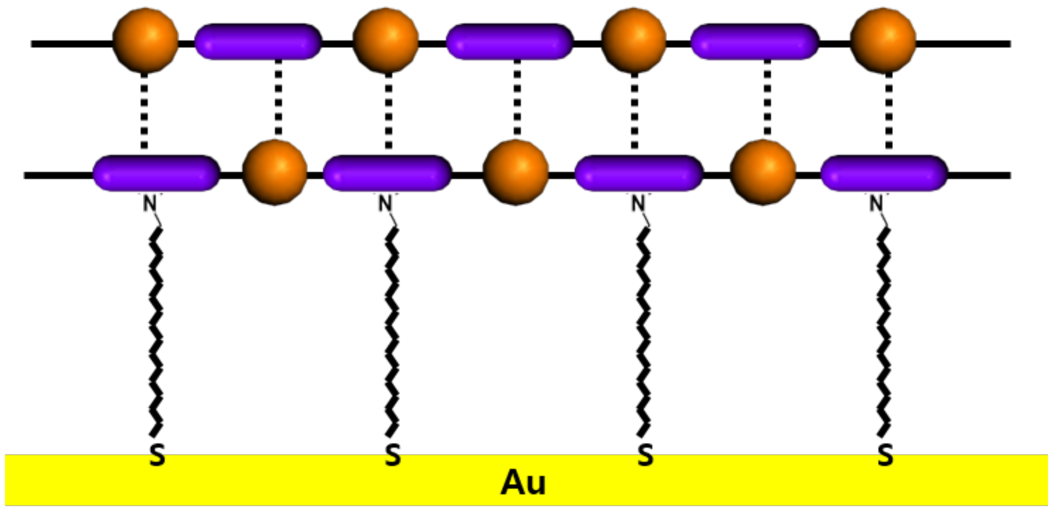


COOH
Terminated

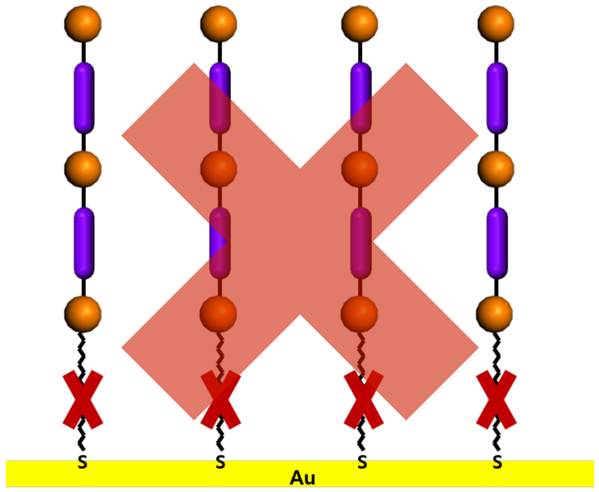
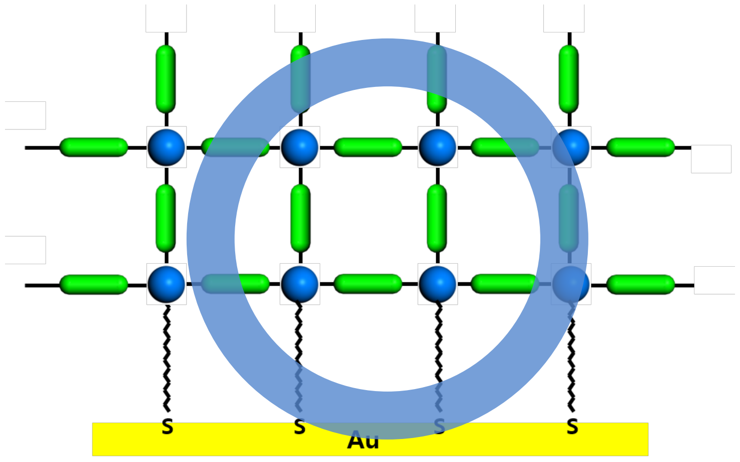
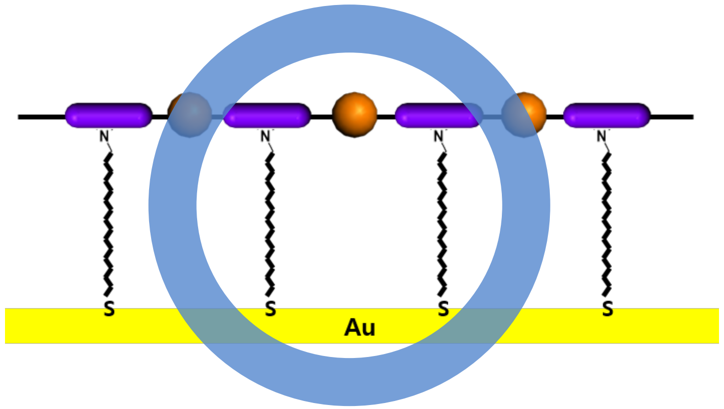


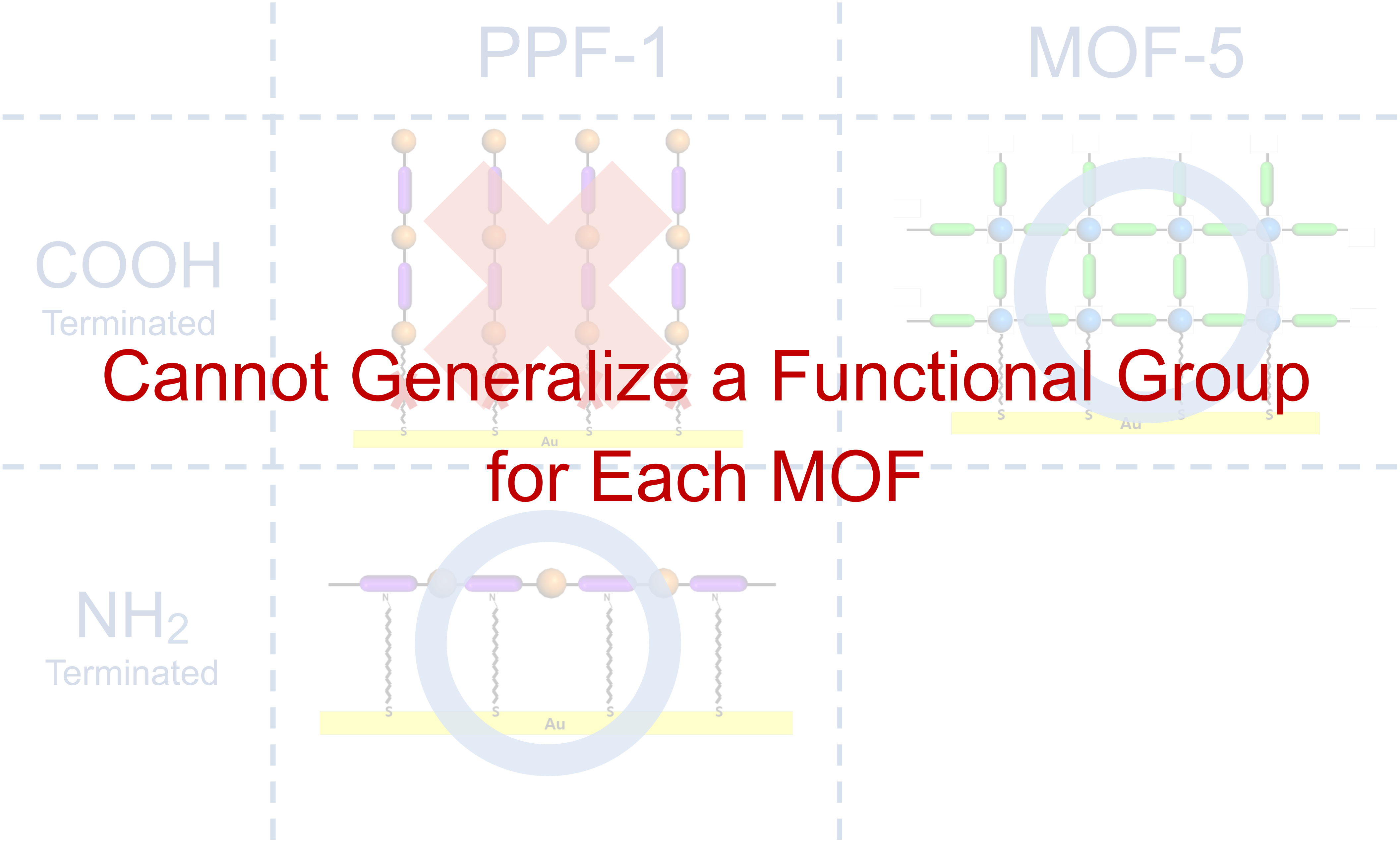
Cannot Withstand weight
(Growth: Perpendicular)

NH_2
Terminated



Can Withstand weight
(Growth: Parallel)

	PPF-1	MOF-5
COOH Terminated		
NH_2 Terminated		

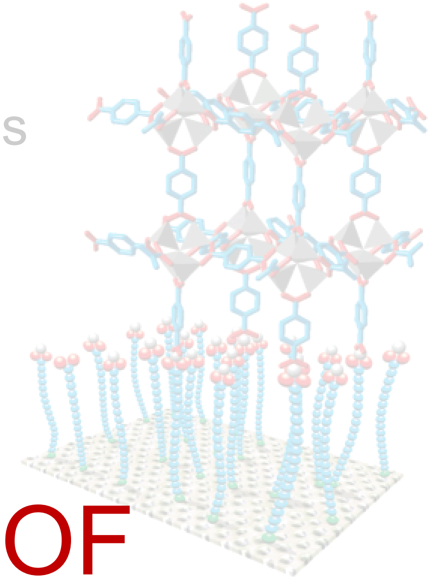


Cannot Generalize a Functional Group for Each MOF

Fabrication of MOF Films

1. layer-by-layer growth

2. Growth/deposition from solvothermal mother solutions



1. Require Specific Substrate

2. Cannot Be Made with Preformed MOF

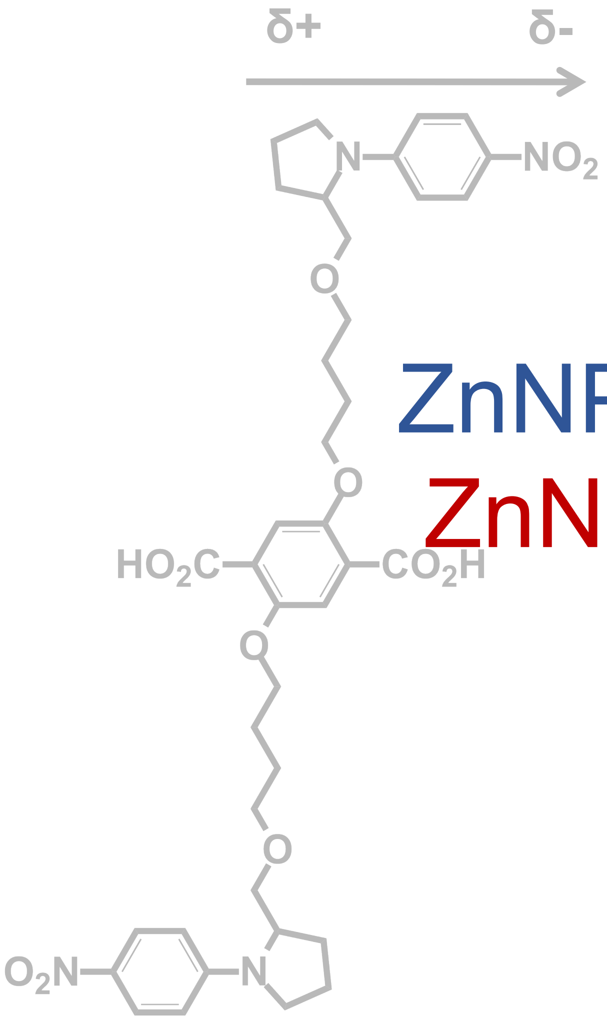
3. microwave-induced t hermal deposition

4. Gel-layer synthesis

Materials 2010, 3, 1302-1315
J. AM. CHEM. SOC. 2005, 127, 13744-13745
Microporous and Mesoporous Materials 123 (2009) 100–106
Angew. Chem. Int. Ed. 2010, 49, 7225 –7228

Molecular Glue

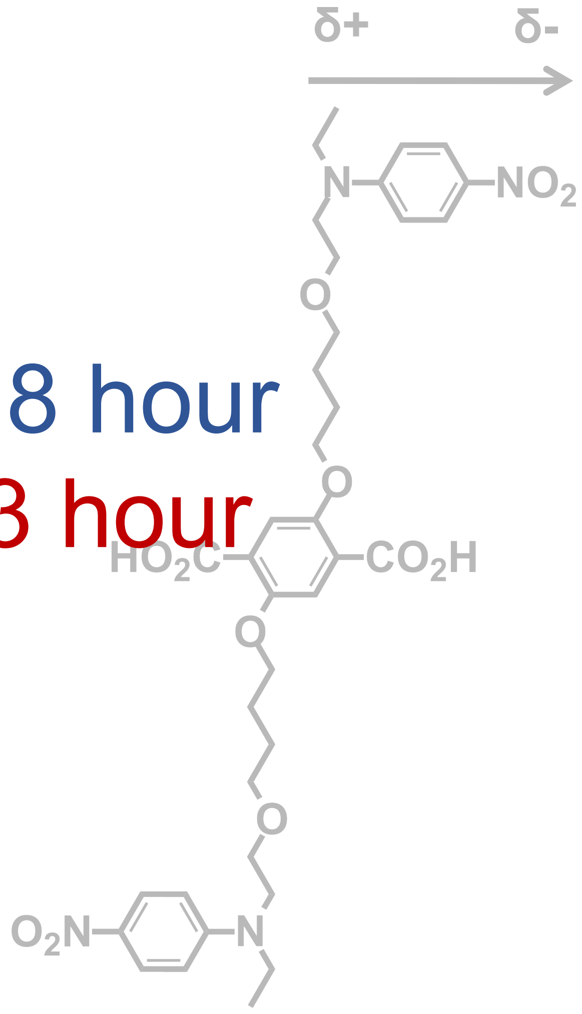
BDC-NPP & BDC-NPE



BDC-NPP

ZnNPP: about 18 hour

ZnNPE: about 3 hour



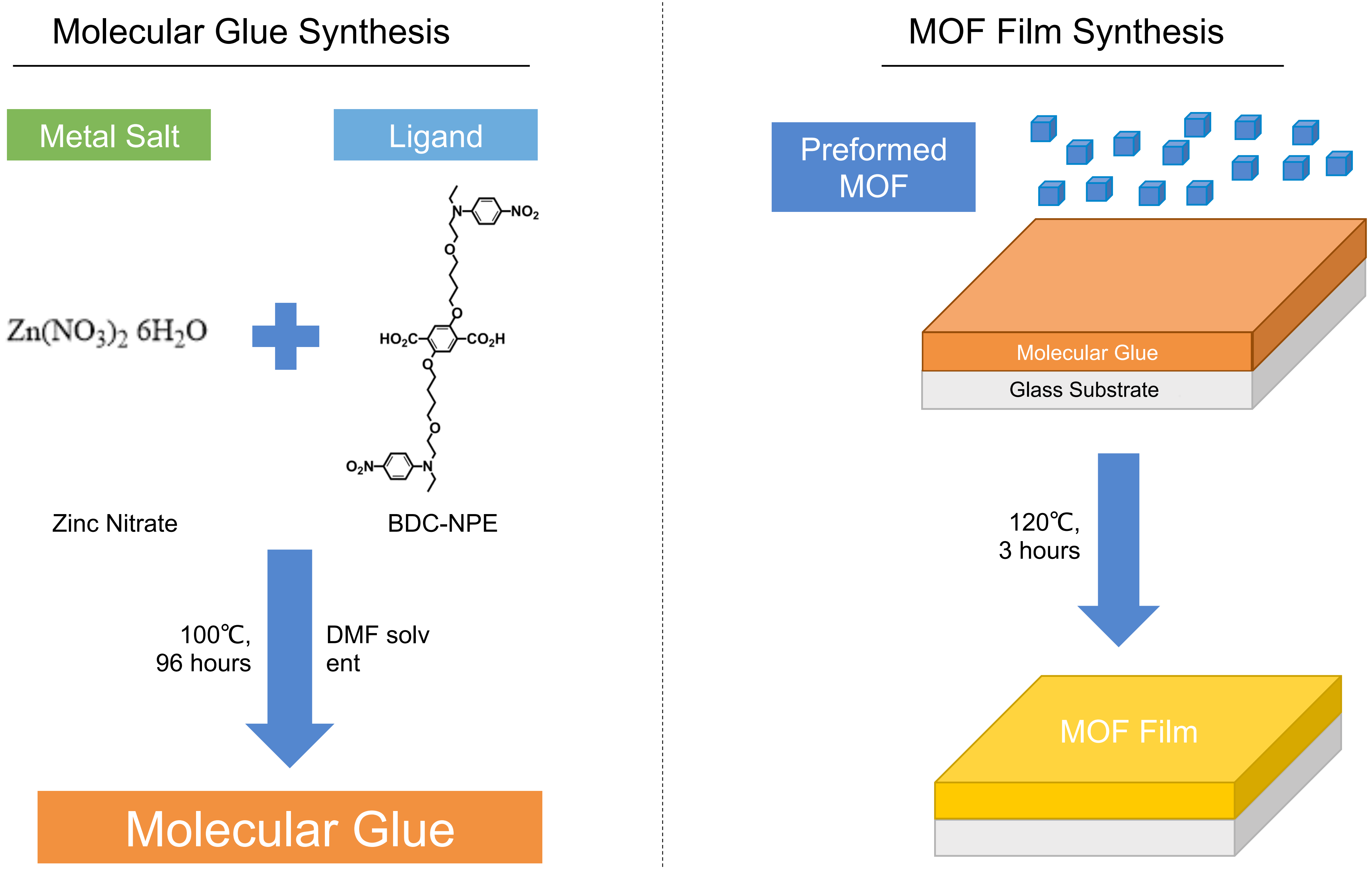
BDC-NPE

Macromol. Theory Simul. 2004, 13, 265–272.

Meaning of Our Research

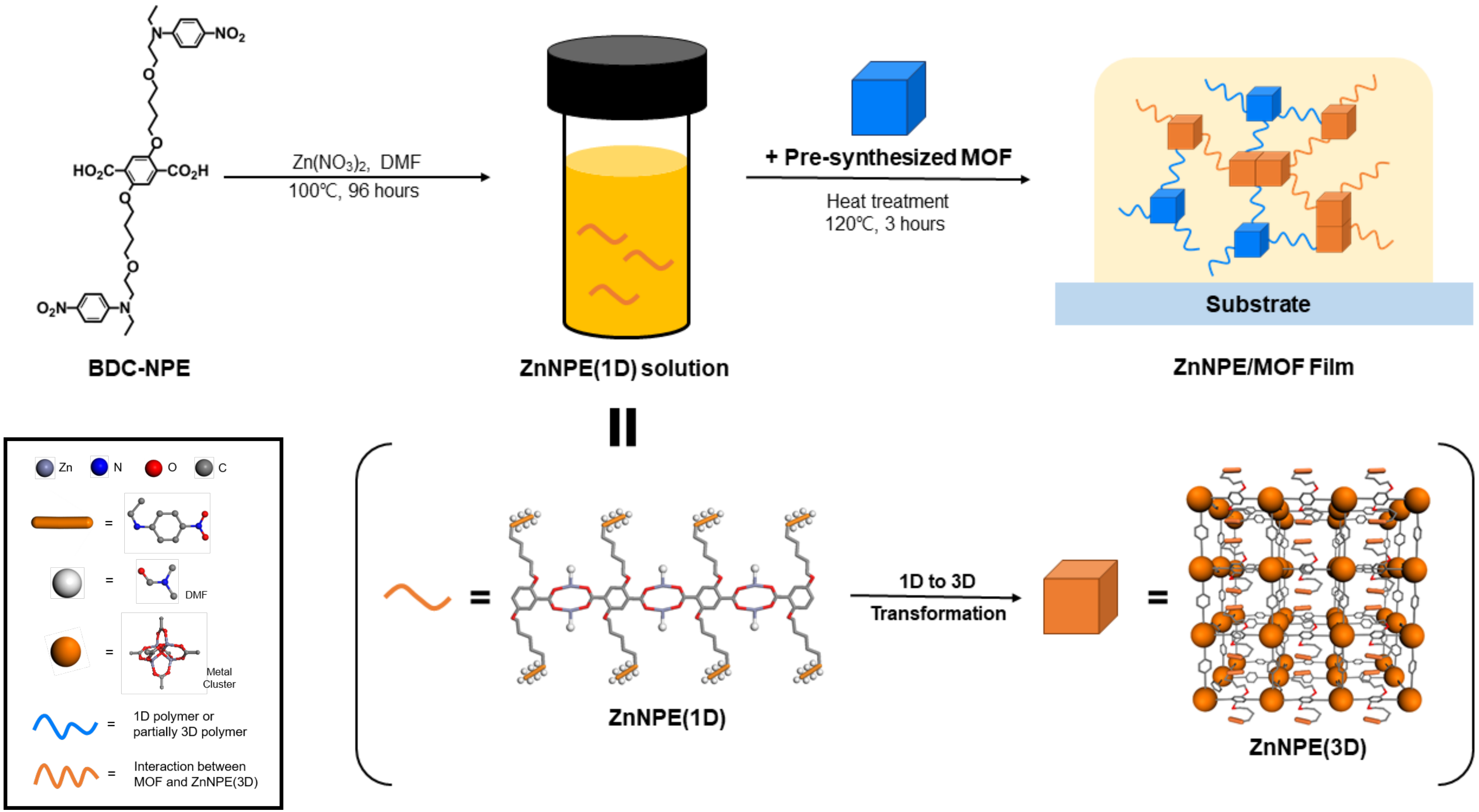
Conventional	Molecular Glue
Form MOF on the substrate	Can use Preformed MOF
Thermally unstable substrates like SAM	Glass Substrate
Cannot attach MOFs that needs to be synthesized at High T	Can attach any kind Of MOF

Synthesis


Molecular Glue Synthesis
Metal Salt
Ligand
$Zn(NO_3)_2$ $6H_2O$
HO_2C
CO_2H
NO_2
O_2N
N
O
Zinc Nitrate
BDC-NPE
100℃,
96 hours
DMF solv
ent
Molecular Glue
MOF Film Synthesis
Preformed
MOF
Molecular Glue
Glass Substrate
120℃,
3 hours
MOF Film

Result & Discussion

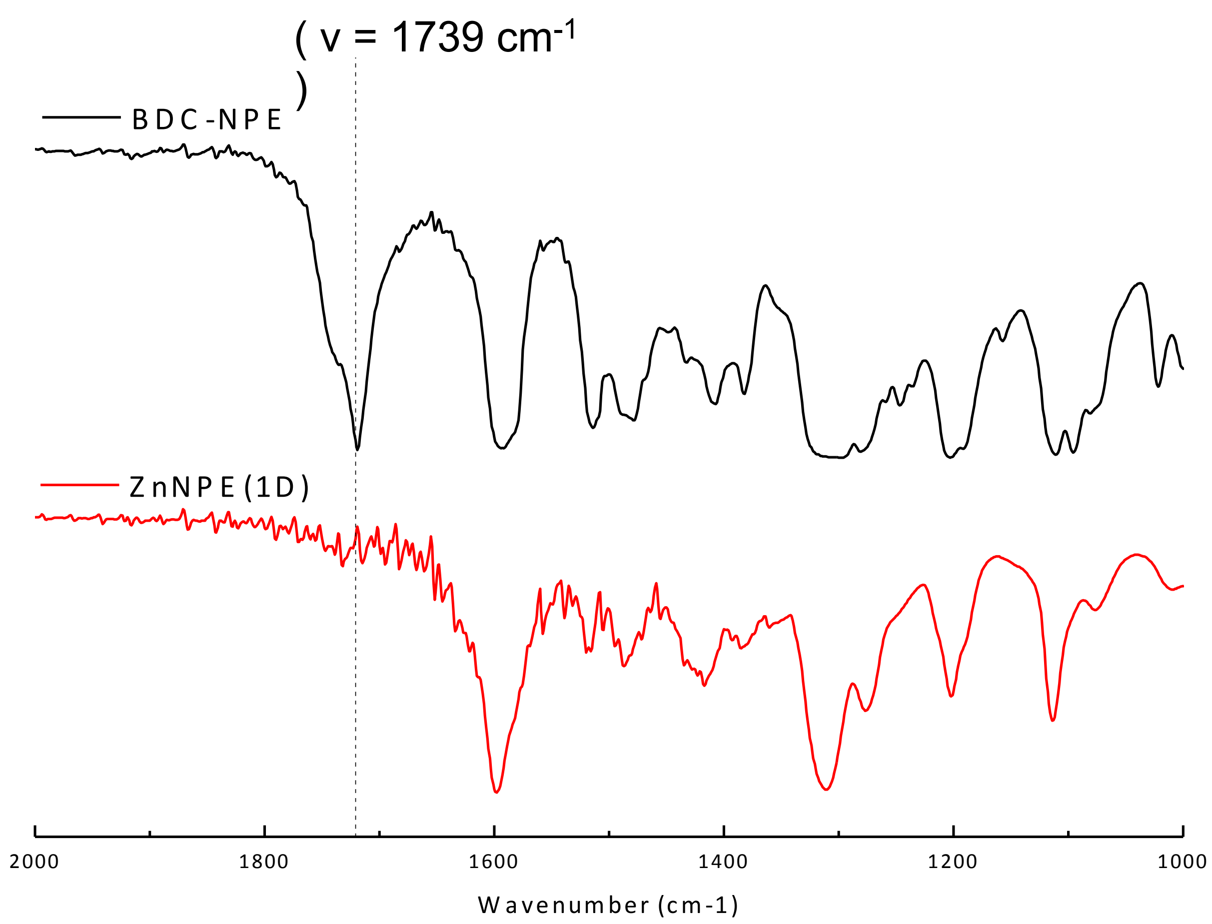
Scheme



NO_2
HO$_2$C
CO_2H
O_2N
N
O
Zn(NO$_3$)$_2$, DMF
100℃, 96 hours
+ Pre-synthesized MOF
Heat treatment
120℃, 3 hours
Substrate
BDC-NPE
ZnNPE(1D) solution
ZnNPE/MOF Film
Zn
N
O
C
DMF
Metal Cluster
1D polymer or partially 3D polymer
Interaction between MOF and ZnNPE(3D)
ZnNPE(1D)
1D to 3D
Transformation
ZnNPE(3D)

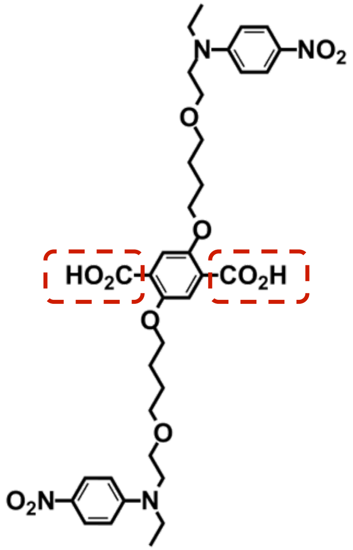
Identification

Infrared Spectroscopy



$1739\ cm^{-1}$

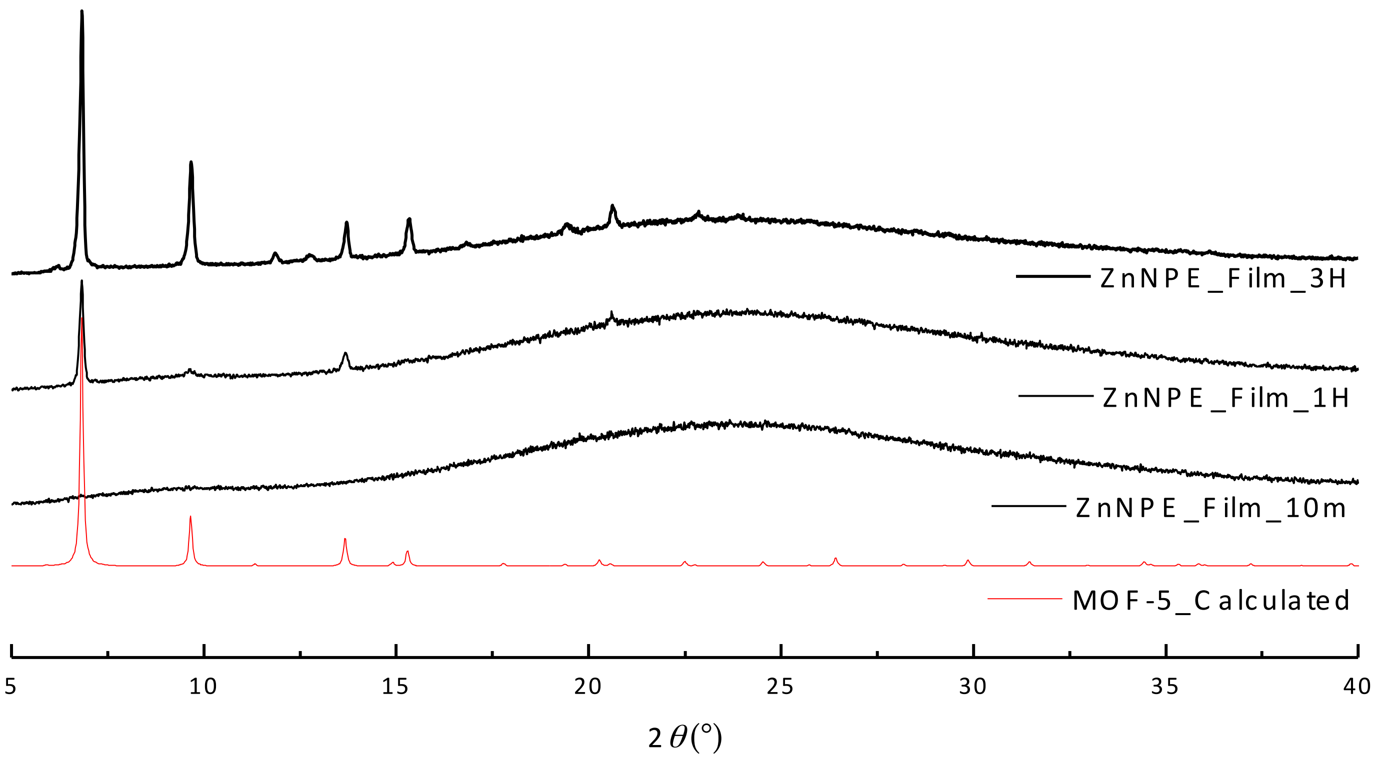
Stretching Vibration of COOH molecule



Identify the coordination of BDC-NPE and Zinc Cluster

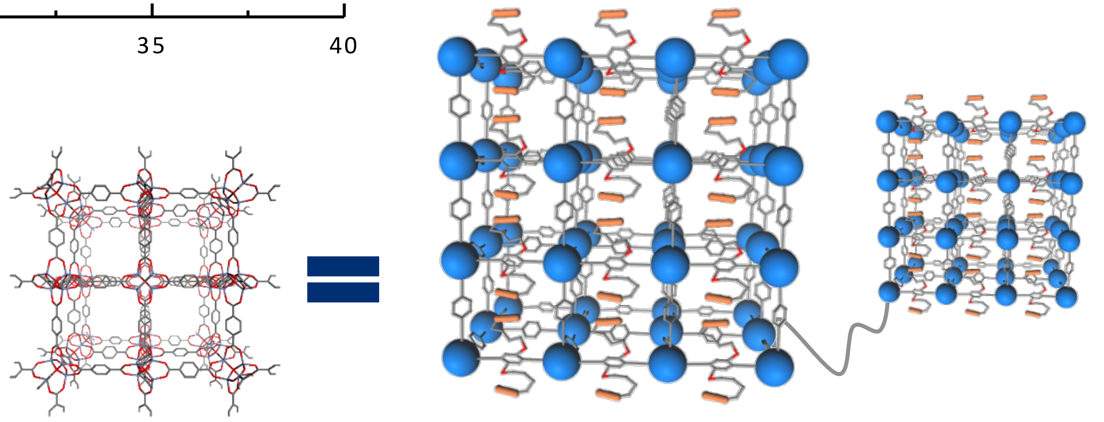
Identification

Powder X-Ray Diffraction

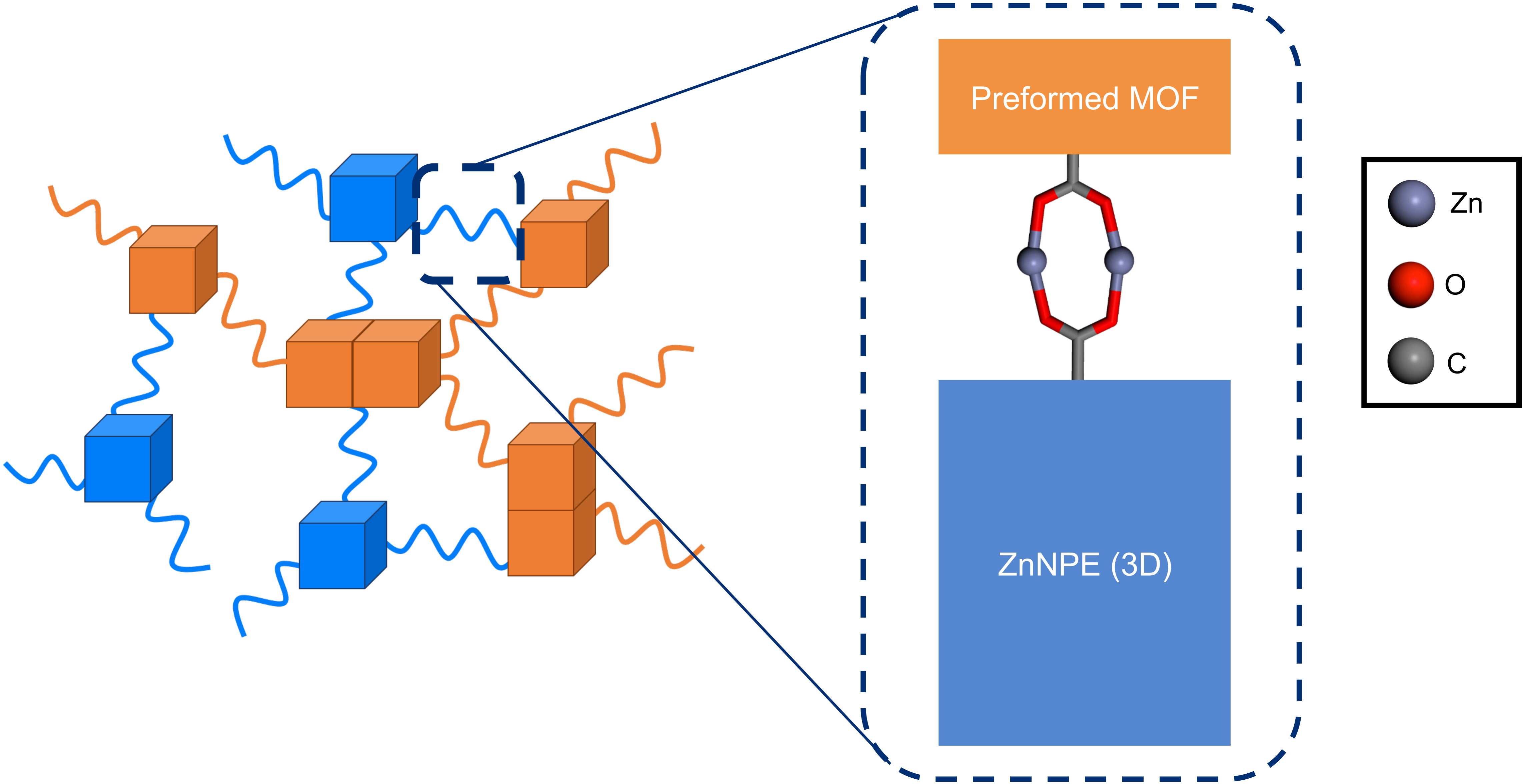


PXRD pattern
Of **MOF-5**
=
PXRD pattern
Of **ZnNPE(3D)**

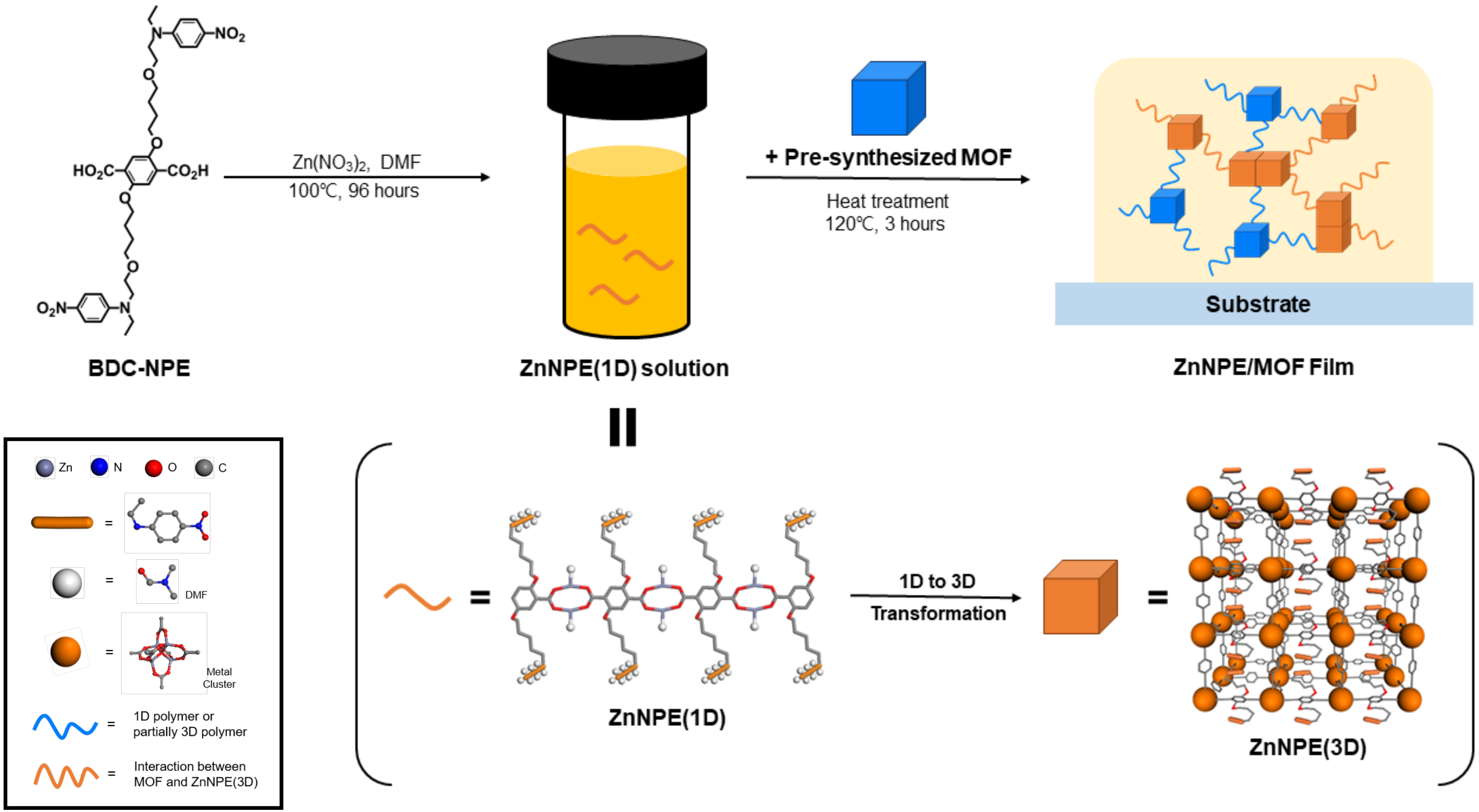
Identify the transformation from 1D to 3D



Interaction of ZnNPE(3D)



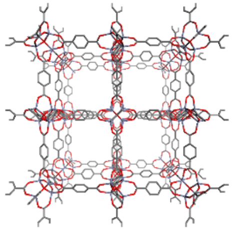
Scheme

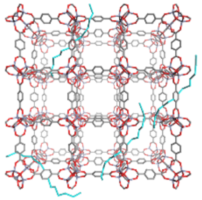


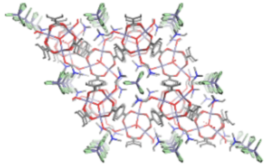
NO2
O
O
HO2C
CO2H
O
O
O2N
N
N
Zn(NO3)2, DMF
100℃, 96 hours
+ Pre-synthesized MOF
Heat treatment
120℃, 3 hours
Substrate
BDC-NPE
ZnNPE(1D) solution
ZnNPE/MOF Film
Zn
N
O
C
DMF
Metal Cluster
1D polymer or partially 3D polymer
Interaction between MOF and ZnNPE(3D)
1D to 3D Transformation
ZnNPE(1D)
ZnNPE(3D)

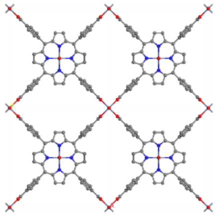
Film-Forming Ability

Incorporated MOF


MOF-5 (Cubic)


MBC5(1:1) (Cubic)


MOF-235 (Octahedral)


PPF-1 (2D nanosheet)

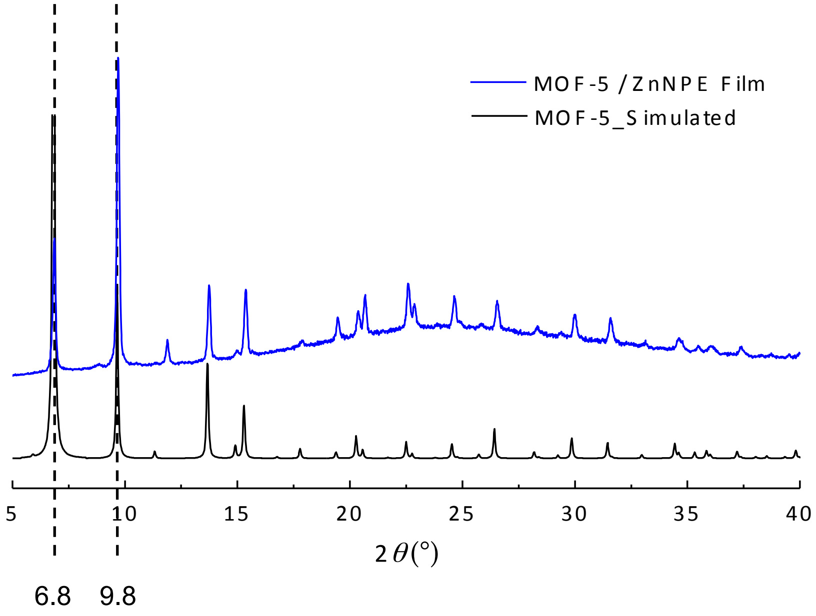
Identification Method

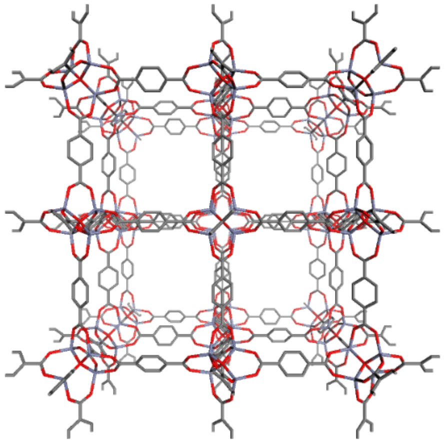
Powder X-Ray Diffraction (PXRD) → Morphology of Crystal

Scanning Electron Microscopy (SEM) → Top/Side View of Film

MOF-5 Incorporated Film

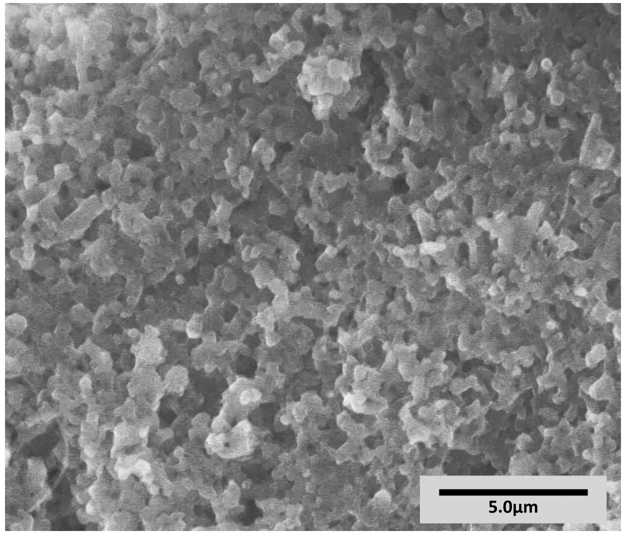
Powder X-Ray Diffraction (PXRD)



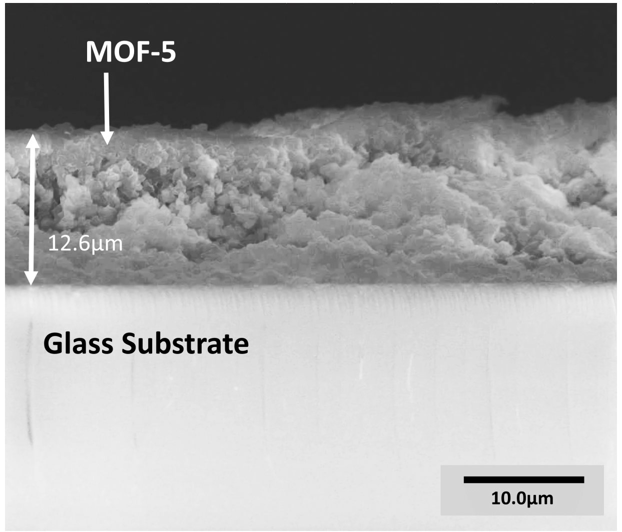


MOF-5 Framework

Scanning Electron Microscopy (SEM)



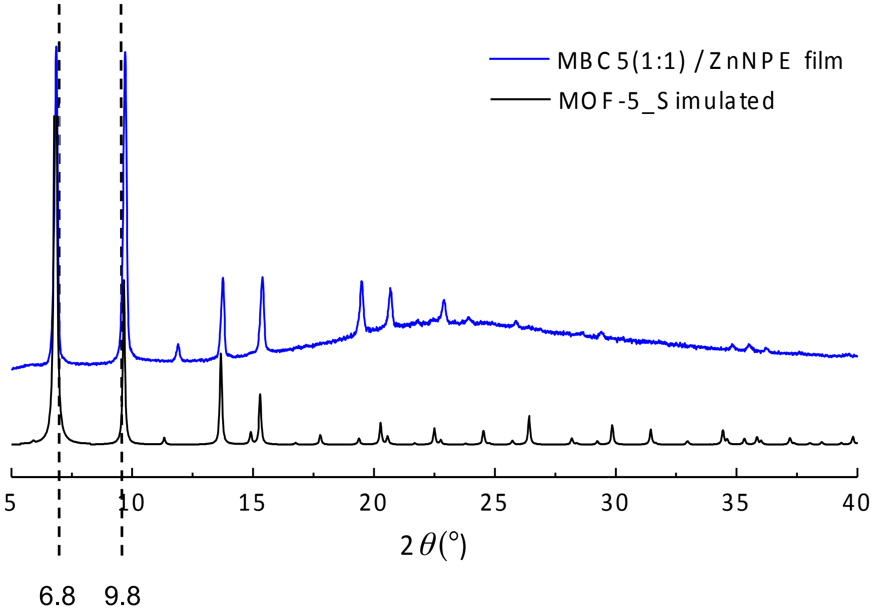
Top View

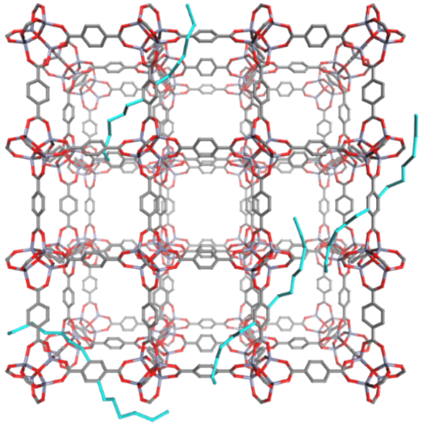


Cross-Sectional View

MBC5(1:1) Incorporated Film

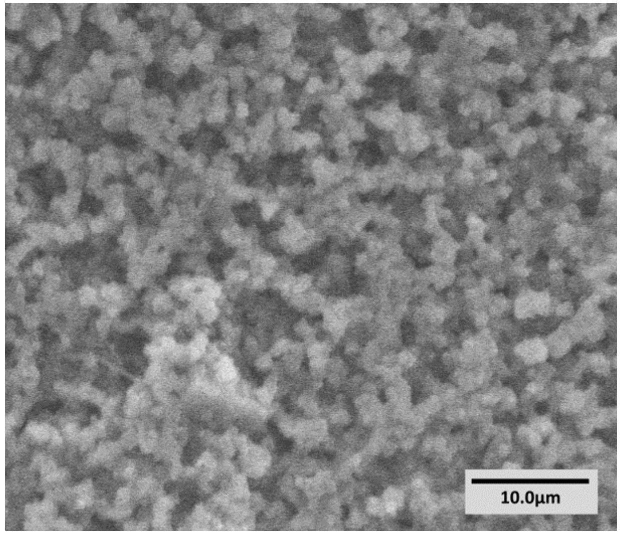
Powder X-Ray Diffraction (PXRD)



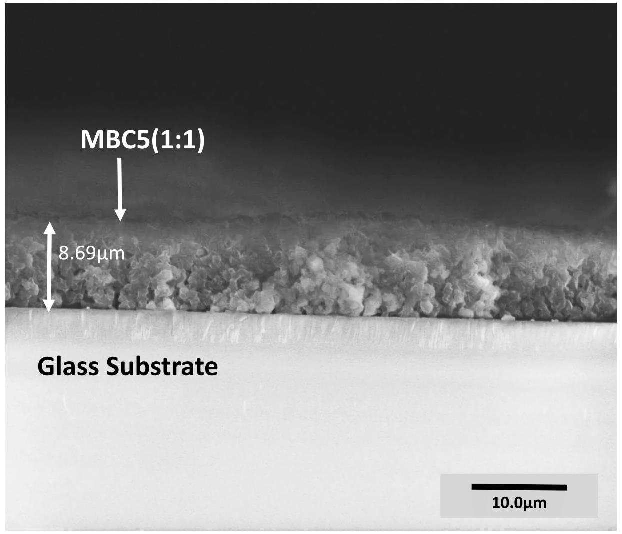


MBC5(1:1)
Framework

Scanning Electron Microscopy (SEM)



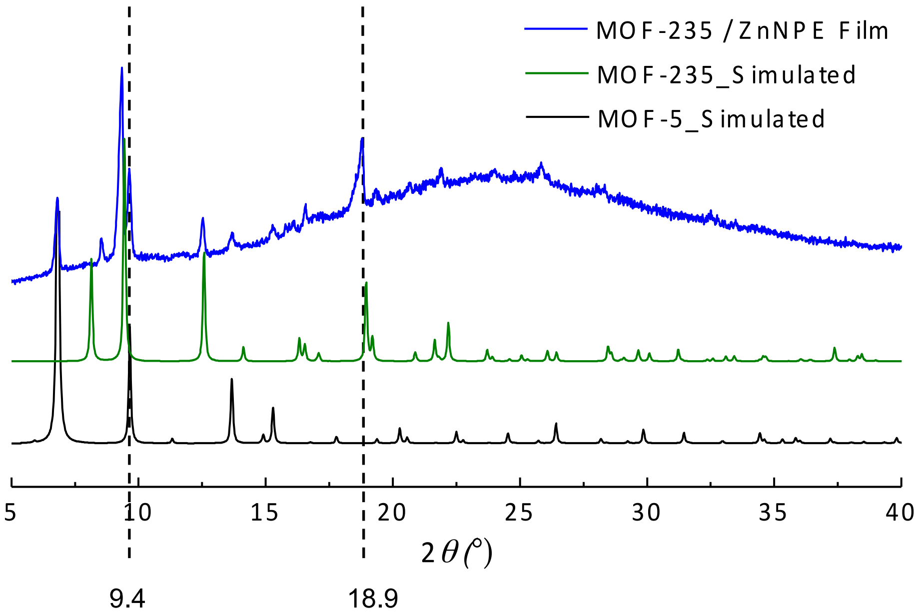
Top View

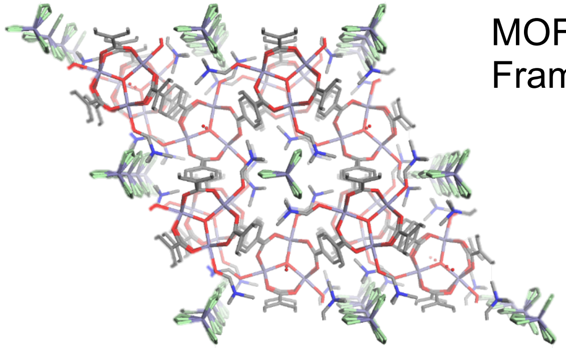


Cross-Sectional View

MOF-235 Incorporated Film

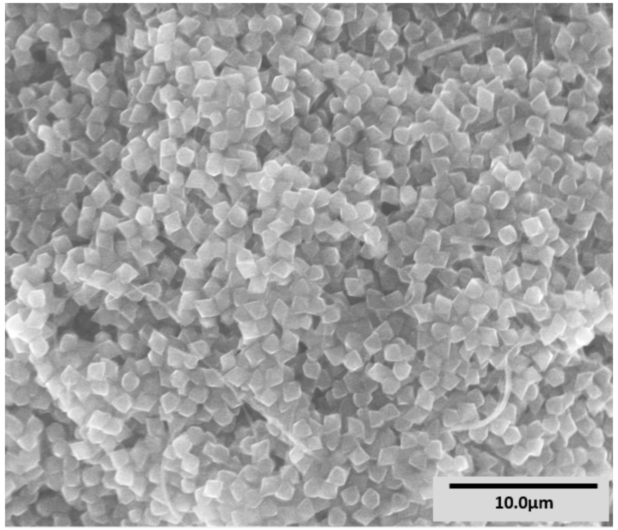
Powder X-Ray Diffraction (PXRD)



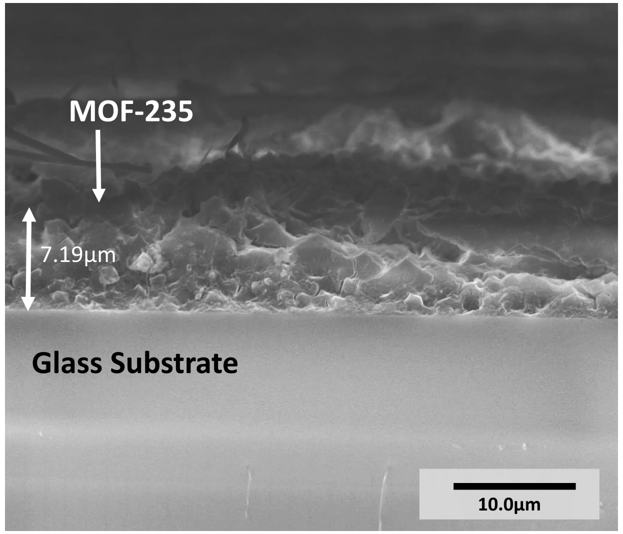


MOF-235
Framework

Scanning Electron Microscopy (SEM)



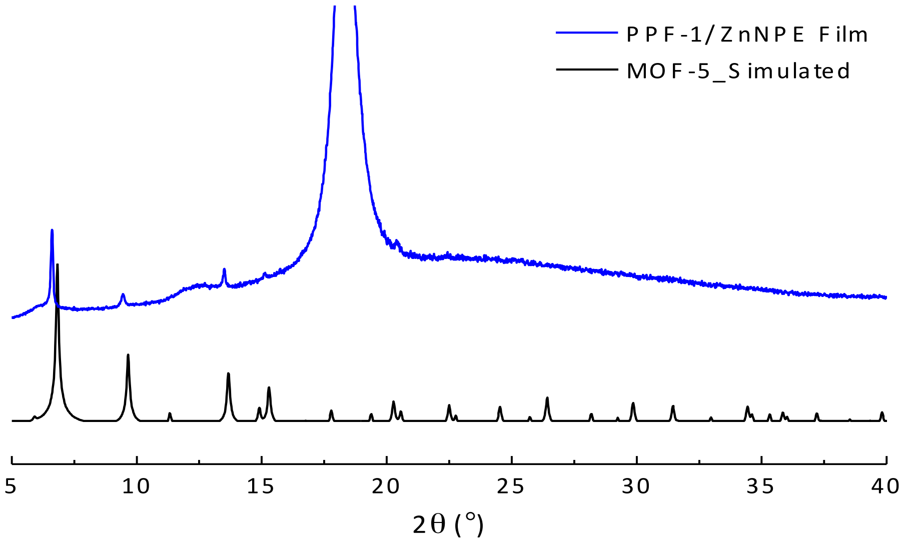
Top View

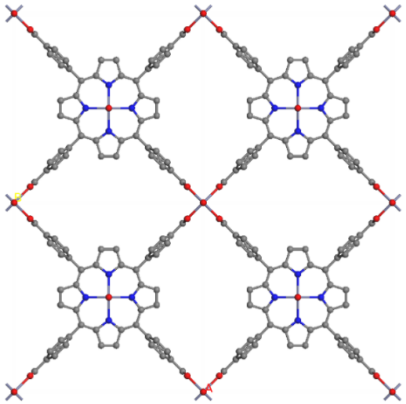


Cross-Sectional View

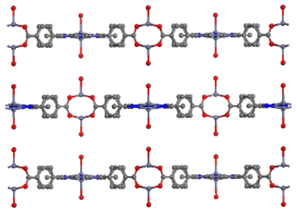
PPF-1 Incorporated Film

Powder X-Ray Diffraction (PXRD)

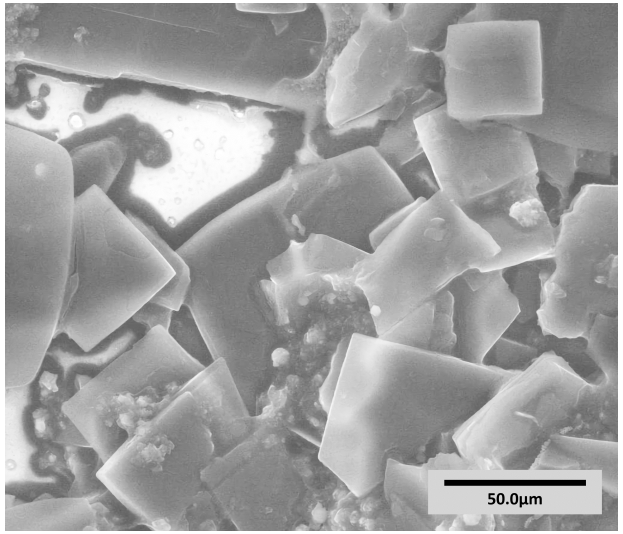




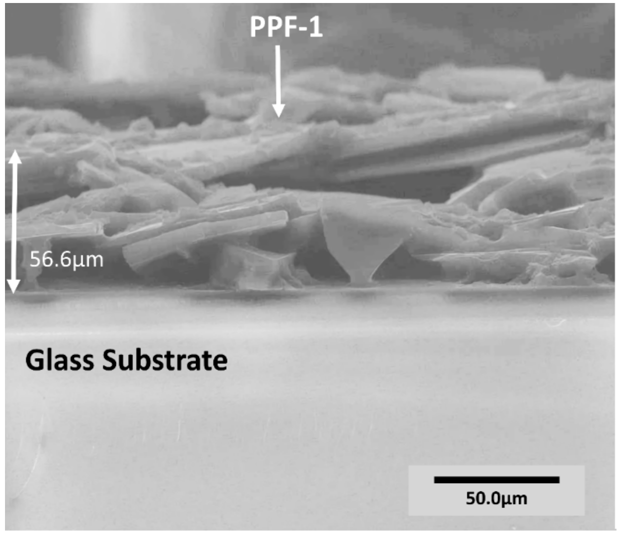
PPF-1
Framework



Scanning Electron Microscopy (SEM)



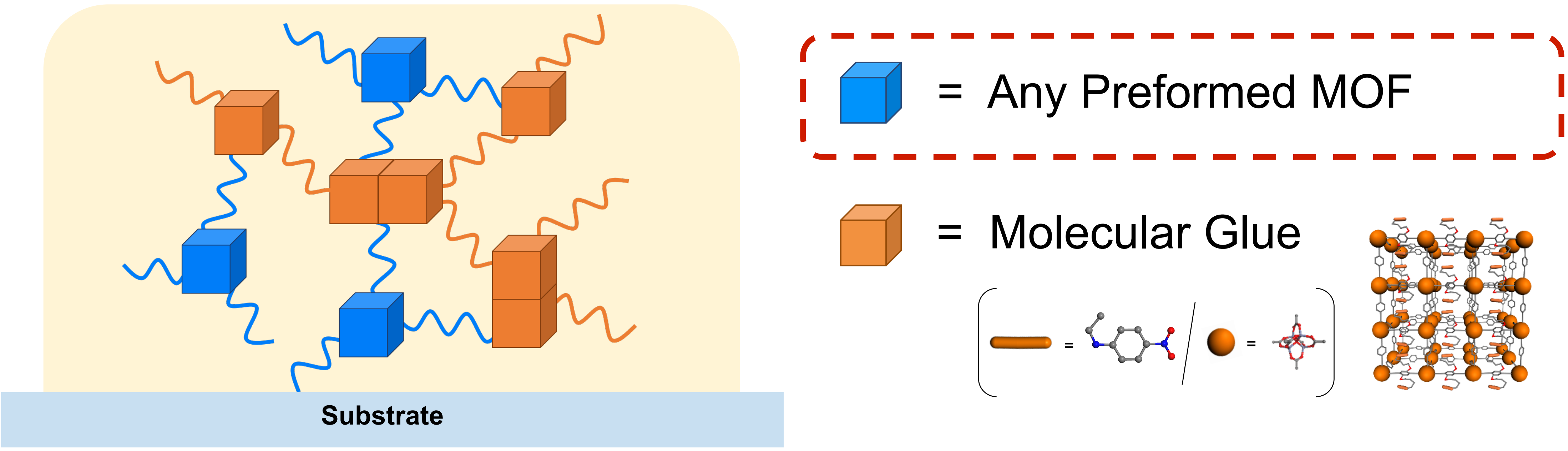
Top View



Cross-Sectional View

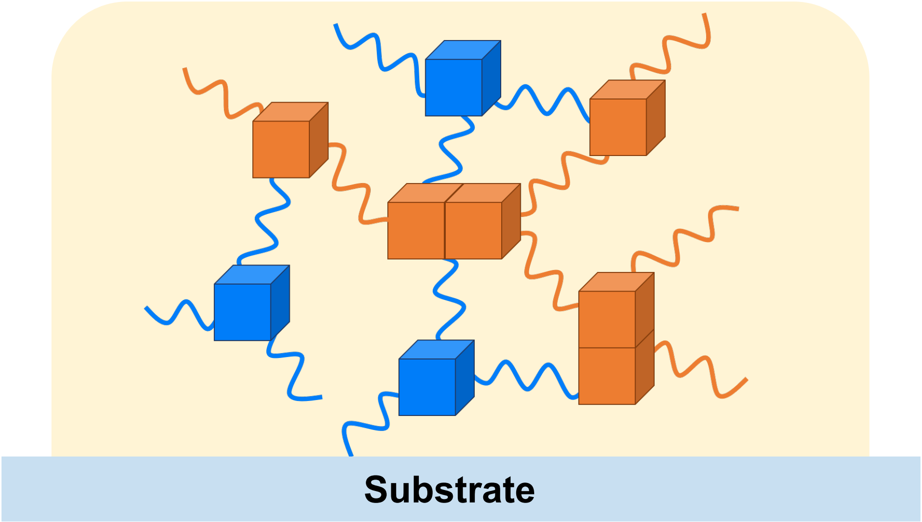
Conclusion

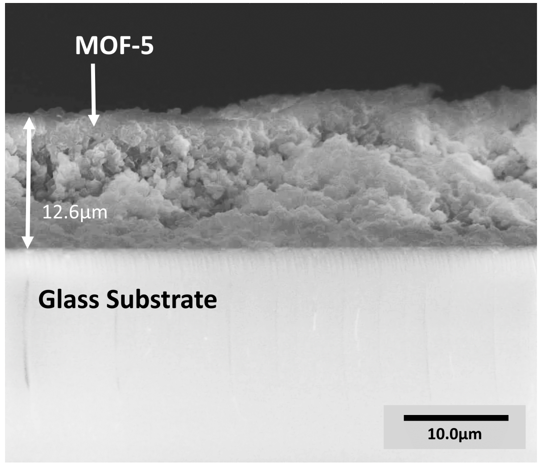
[MOF-Incorporated Film]



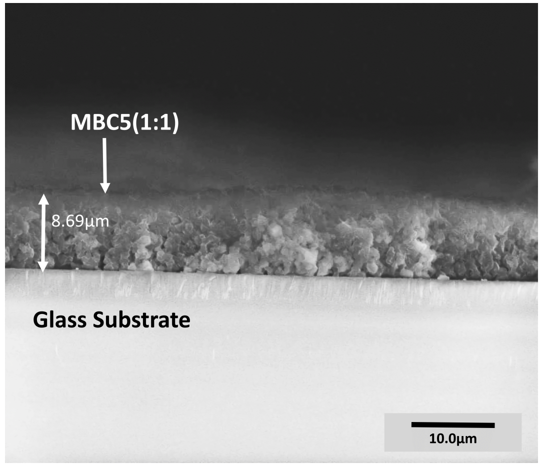
Wide range of Preformed MOF
can be incorporated

MOF-Incorporated Film

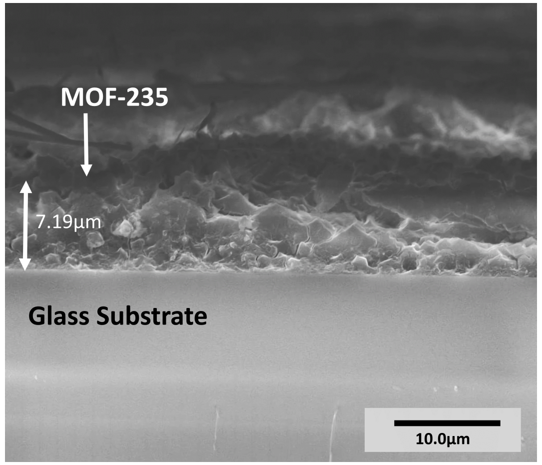




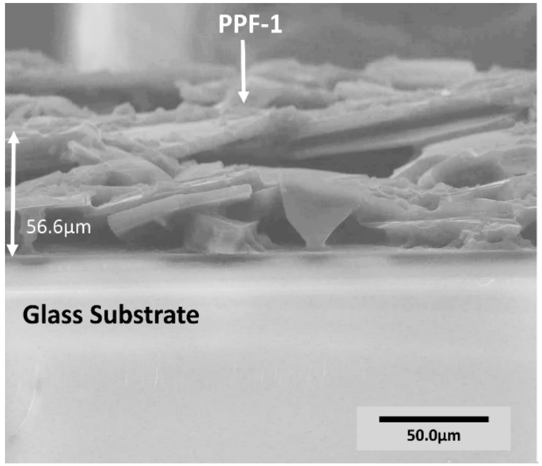
MOF-5



MBC5 (1:1)



MOF-235



PPF-1

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An Entirely New Molecular Glue for MOF Using Unusual Structural Transformation of a Coordination Polymer

Q&A

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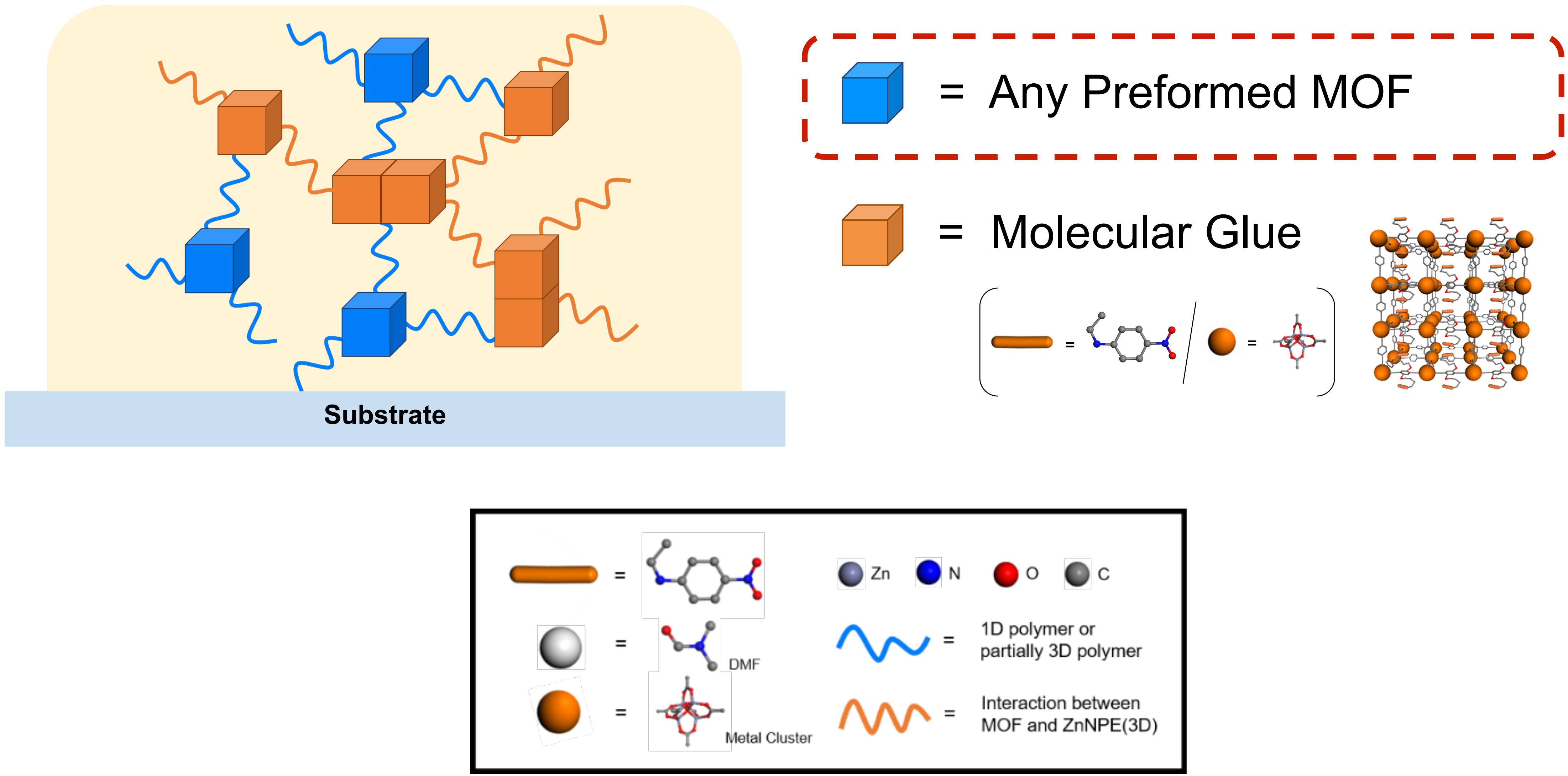
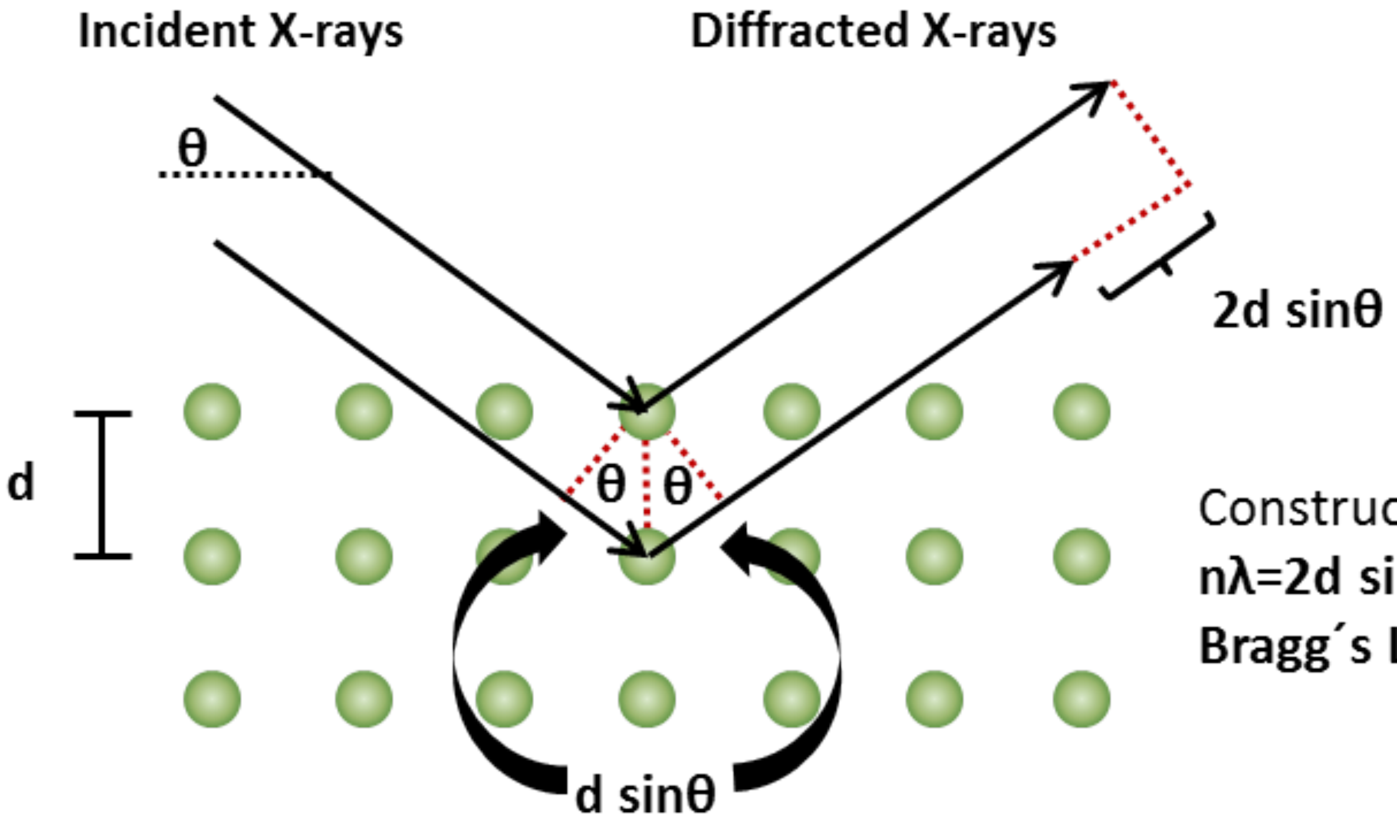

Substrate
= Any Preformed MOF
= Molecular Glue
Zn
N
O
C
DMF
Metal Cluster
1D polymer or
partially 3D polymer
Interaction between
MOF and ZnNPE(3D)

Q1. How does PXRD work?



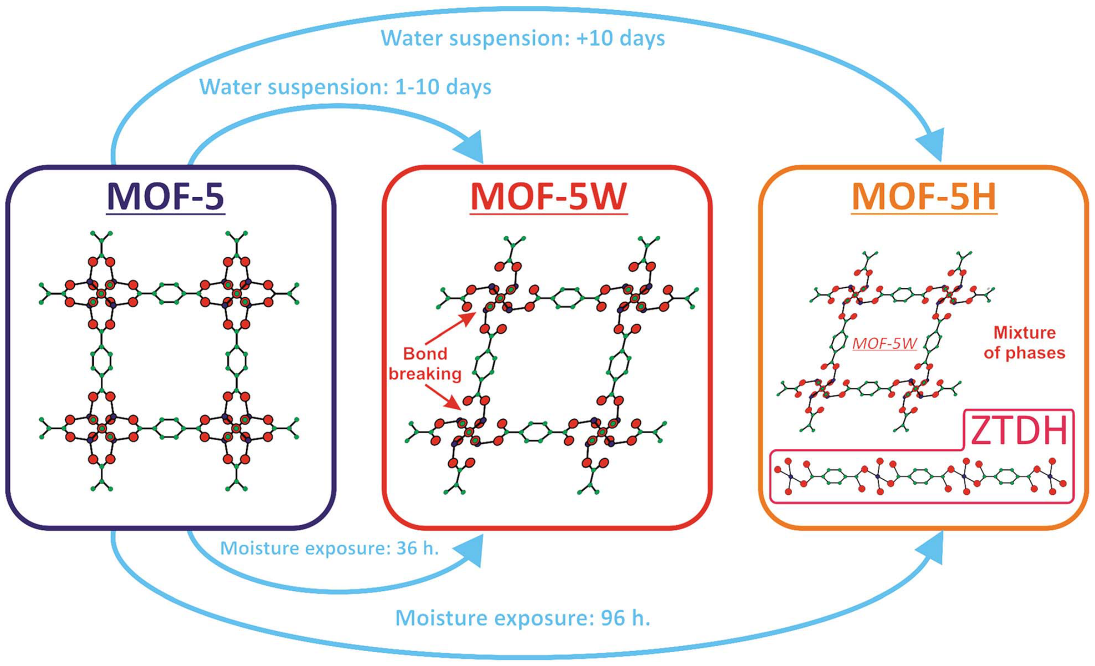
Constructive interference when
$n\lambda = 2d \sin\theta$
Bragg´s Law

Q2. What is CCDC?

The Cambridge Crystallographic Data Centre (CCDC) is a crystallographi c organization based in Cambridge, England. Cambridge Structural Datab ase stores almost every small molecule crystal structures.

Q3. Data of MOF, an unstable structure, measured correctly?

As the time passes, MOF structure changes due to various reasons includ ing water vapor. This change can be detected by certain peaks of PXRD r esults.
e.g., MOF-5 8.8 peak



Q4. Were there previously no ways to attach preformed MOF to a substrate as a film?

Actually, research on preformed MOF film was already done.

But in those research, no interaction between the substrate and MOF was revealed. Therefore, physical durability of the film is doubted.

Q5. Can you control the thickness of the film?

We can change the thickness of the film by regulating the amount o f MOF added to the solution.

Also the size of the preformed MOF crystals affect the thickness, so we can control the film size by controlling the heating time of MOF.

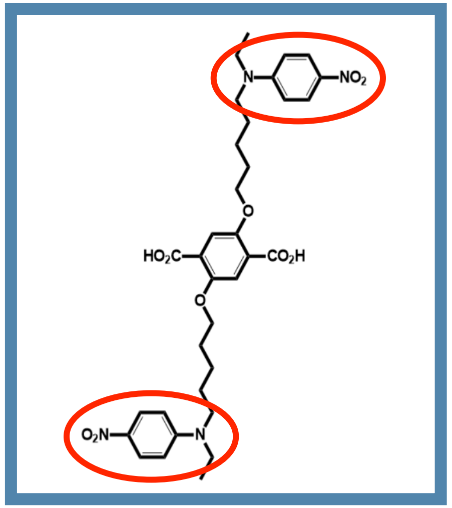
Q6. How is the molecular glue attached to glass?

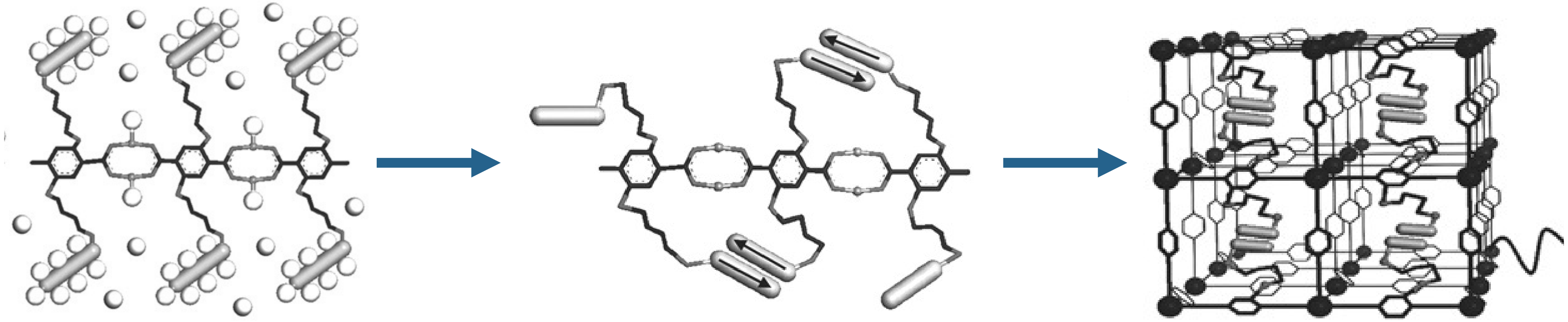
It seems that Molecular Glues' COOH group interacts with the glass subst rates' hydrophilic parts, forming a physically strong film.
There needs further examination of this hypothesis.

Q7. How is the 1D to 3D transformation done?

BDC-NPE contains highly polar push–pull π-conjugated side chains.

This side chain, initially interacting with solvent molecule, interacts with nearby side chain while solvent molecules evaporates during heating.





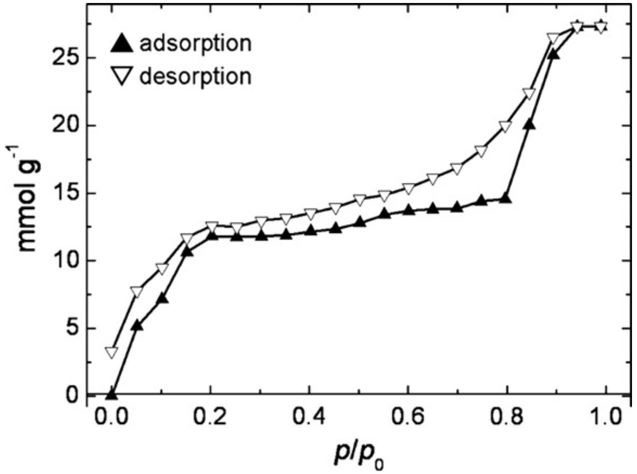
Q8. Difference between previous ZnNPP study?

The topic we researched on was “MOF-Film Forming” using “Molecular Gl ue”. Previous ZnNPP study only tested the film of ZnNPP, using no prefor med MOF, which means that we are the first to test on a function as a mol ecular glue.

Q9. Applications of MOF film? Ex: QCM sensor

MOF Film is used in QCM sensor because of its thin and gas-adsorbing property. Using the frequency of quartz crystals vibration, we can measure the ng-unit mass change of the film.

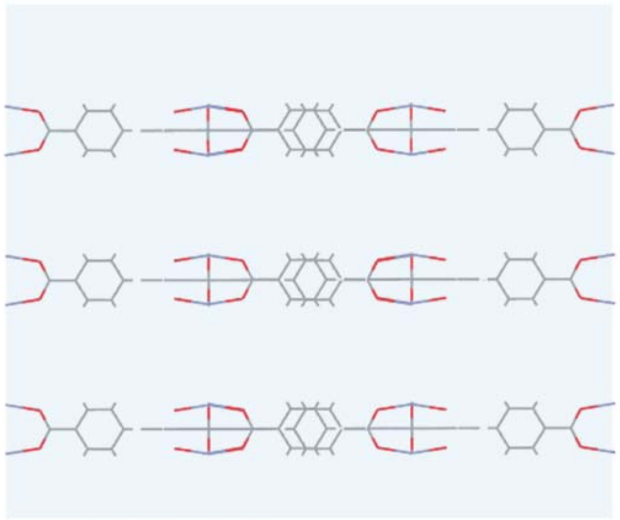
QCM-devices after growth of Cu3(btc)2(H2O)3 xH2O: opaque layer on the SAM-modified gold electrode (left); reference chip without SAM on the gold surface (right).



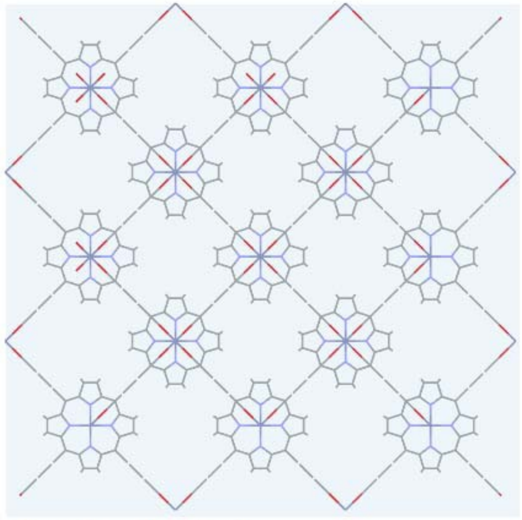
Water-sorption isotherm on a thin film of Cu3(BTC)2, recorded at 294 K with the QCM setup.

Q10. Why didn’t you put the XRD graph of PPF-1 incorporated film?

The orientation of PPF-1 crystal growth effects the XRD graph peaks. PPF-1 crystals we synthesized did not fit the simulated PPF-1 graph.



(h, k, l) = (1, -1, 0)



(h, k, l) = (0, 0, 2)

Q11. How expensive are the substrates used in previous methods?

Silicon wafer: 대략 180,000원

Aluminum Single Crystal Substrate: 103,265원

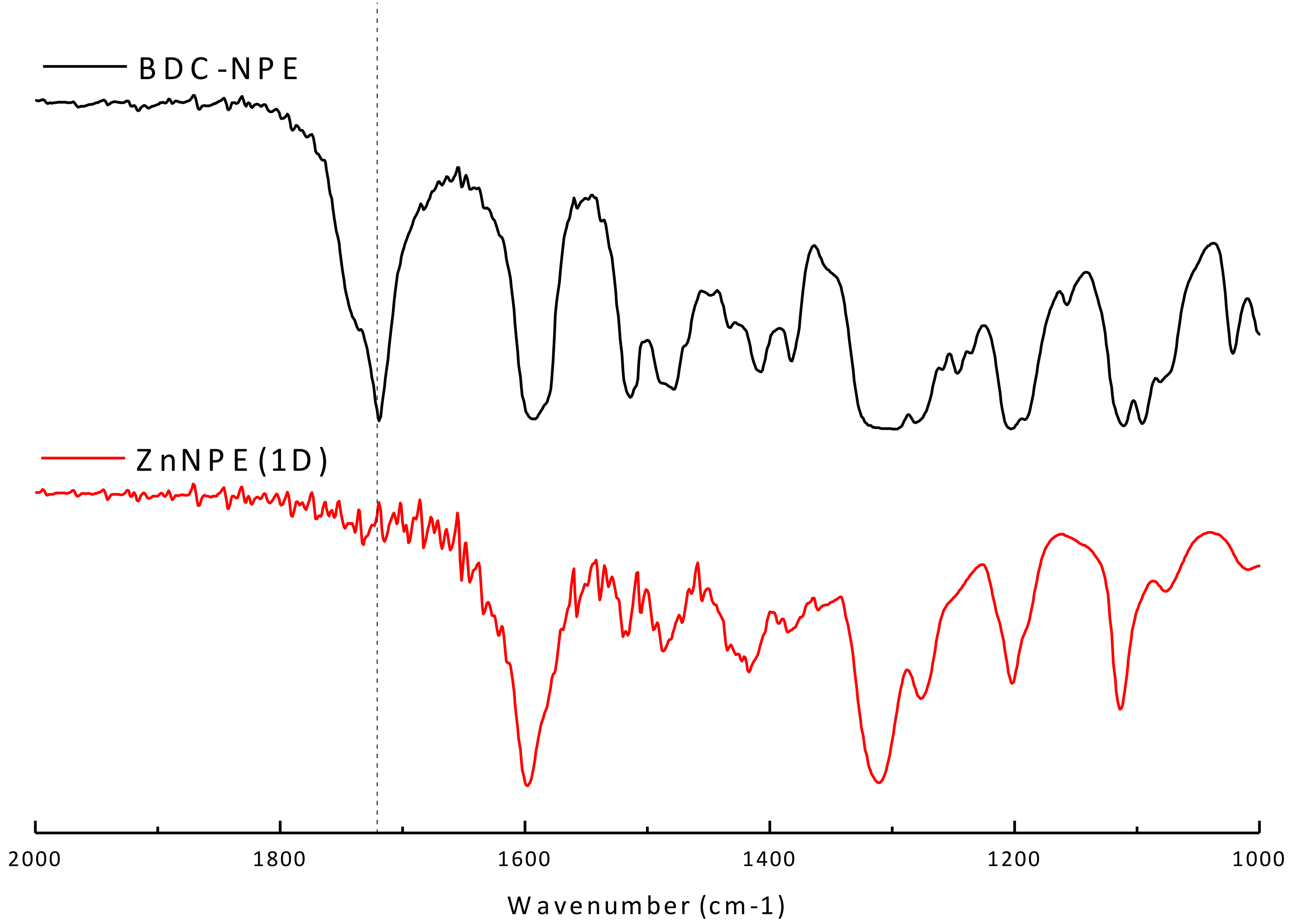
Au (Gold) Single Crystal Substrate: 1,625,065원

Aluminosilicate Glass Slides 10nm Gold (Au) over 2nm Ti Adhesion Layer - 1 inch x 3 inch x 0.7mm

: 423,930원

Cover glass 18 mm x 18 mm 1000ea/pk: 26,400원

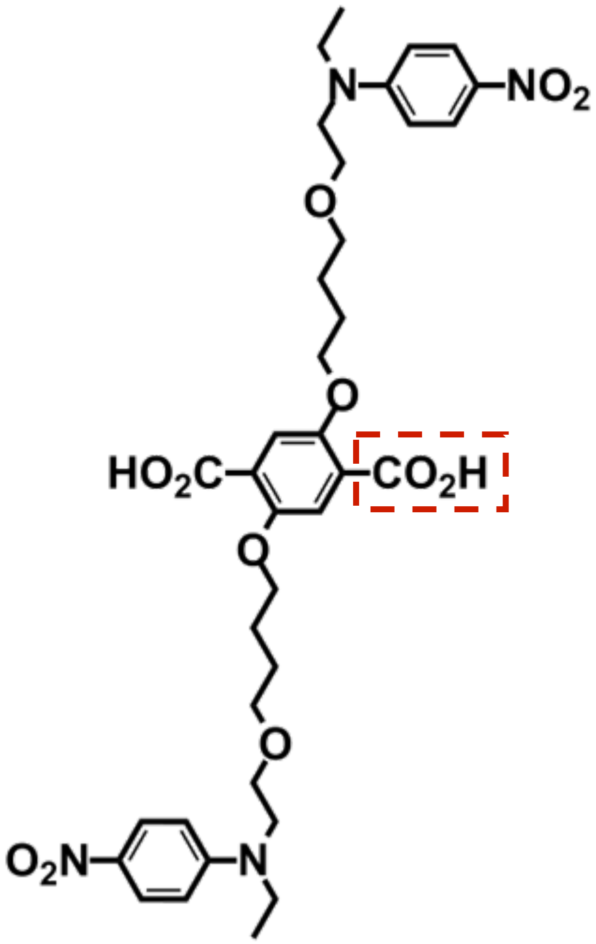
Q12. Analysis about other peaks on IR?



Peak on 1739cm-1 are enough to verify the syn thesis of ZnNPE(1D)

Other peaks are not nec essary to identification

Q13. COOH group is always the terminal part of MOF ?



Depends on the situation

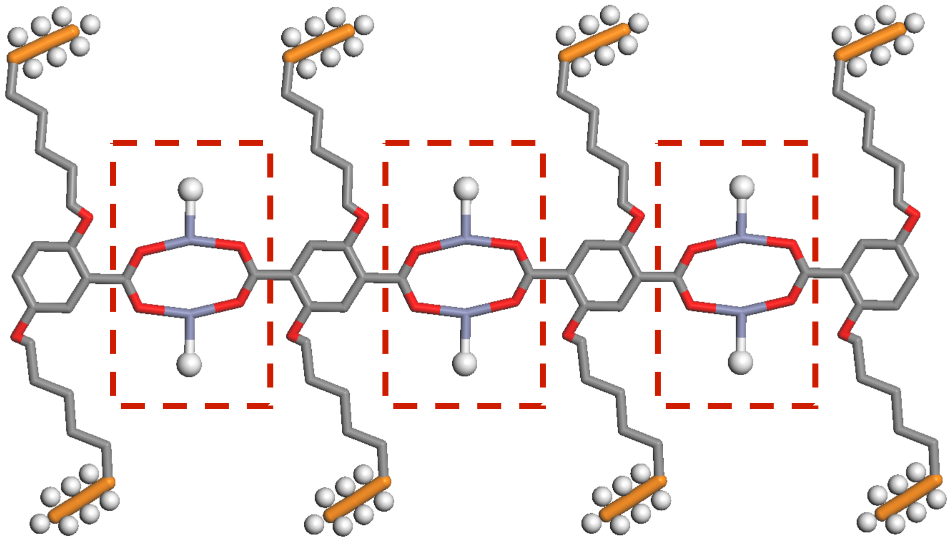
Terminal part can be a metal coordinated with othe r molecules (Ex. Water, DMF)
⇒Not stable, When excess metal is added

Mostly, terminal part would be carboxylate group

Q14. Verify interaction between ZnNPE(3D) and MOF?

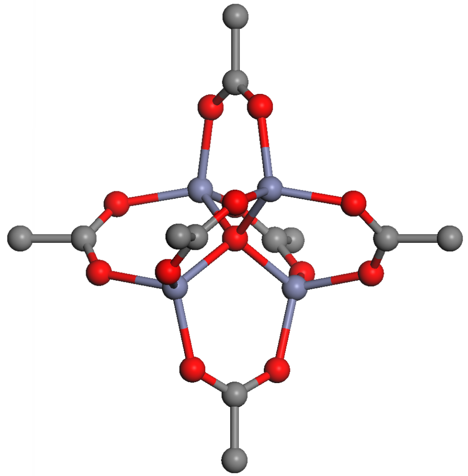
* Interaction between zinc metal and carboxylate group is spontaneous process and strong.

* It is natural for carboxylate group to bind to vacant coordination site of zinc metal



Carboxylate Group

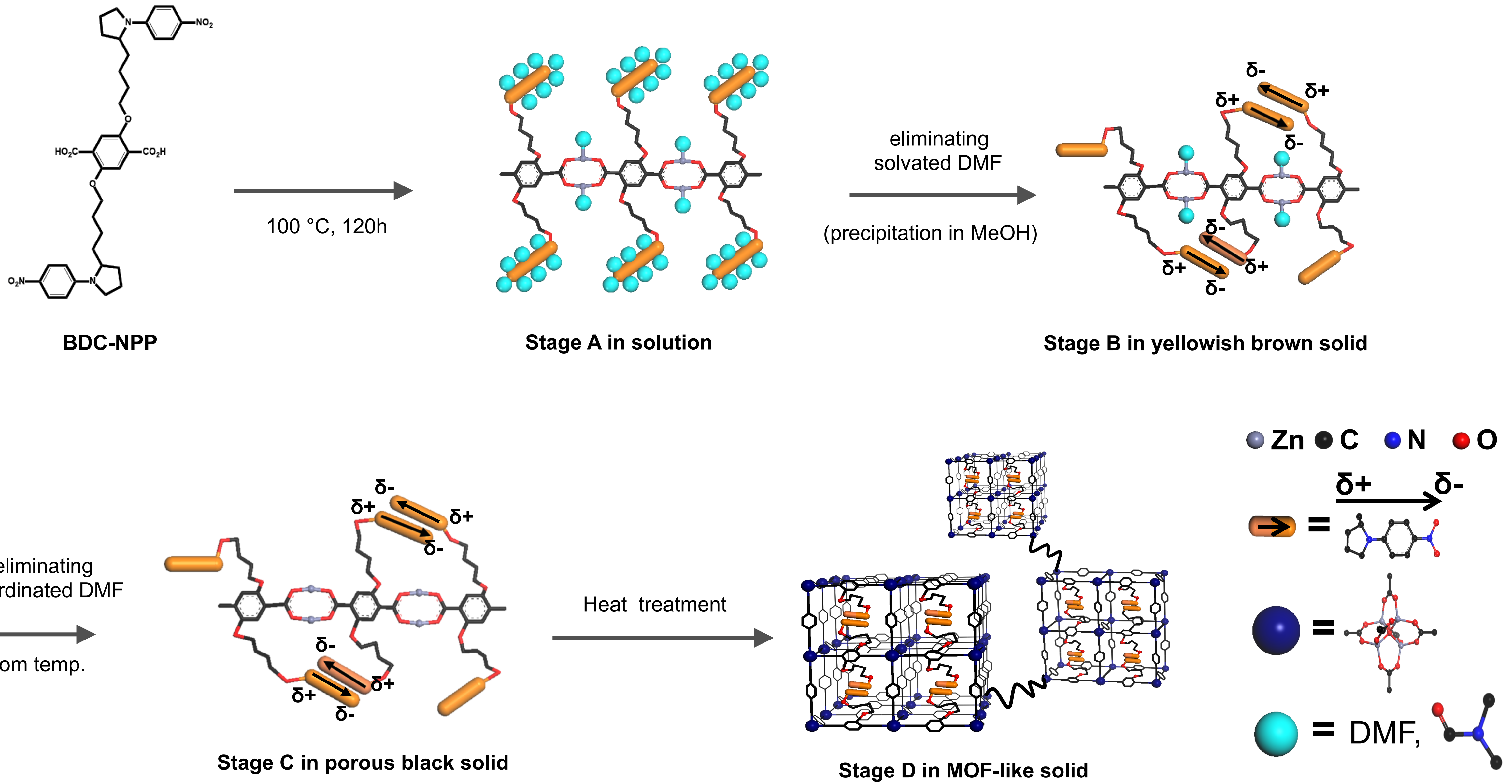
Binds to an vacant
Coordination site



Q15. How do you know that the cubic structure in the surface of your film is MOF-5, when ZnNPE and MOF-5 is isoreticular with each other?

When we form a film with just the ZnNPE solution, we can see that there are no visible crystal structure on the surface of the film.

Q16. Preceding Research



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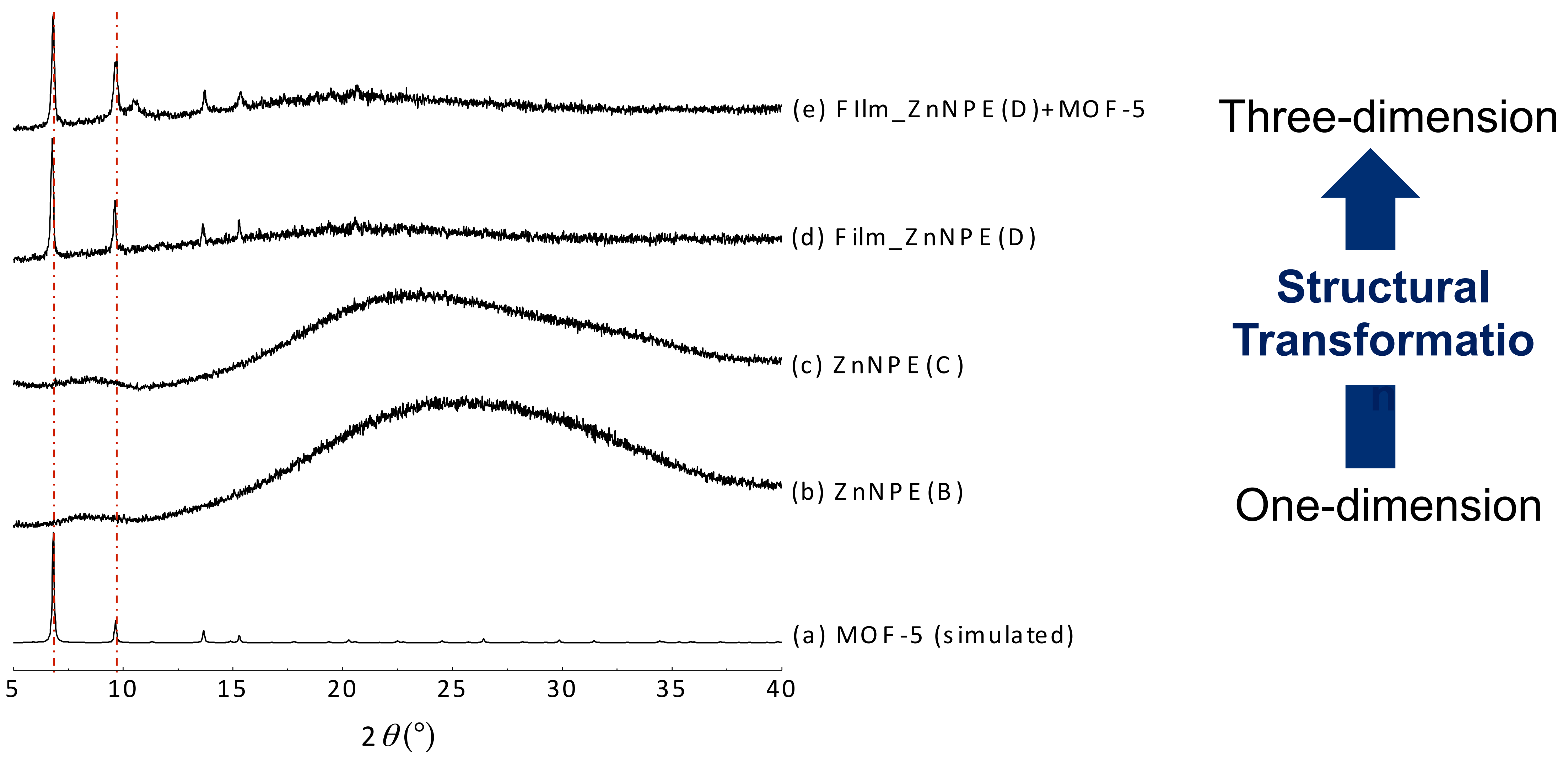
Q17. XRPD results



How to widen application & usage of MOF?

[MOF-Incorporated Film]