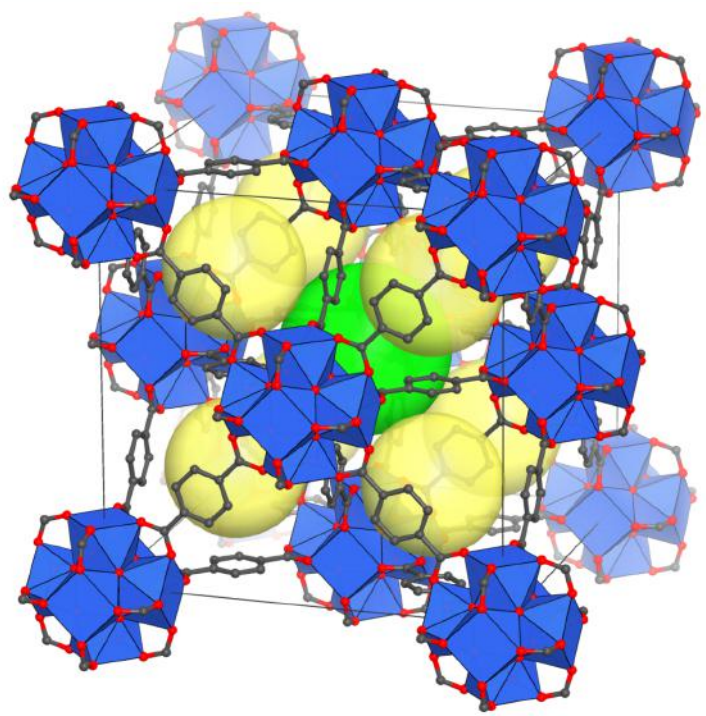
The Synthesis of Metal-Organic Frameworks (MOFs) and Recent Advances in MOF Catalysis



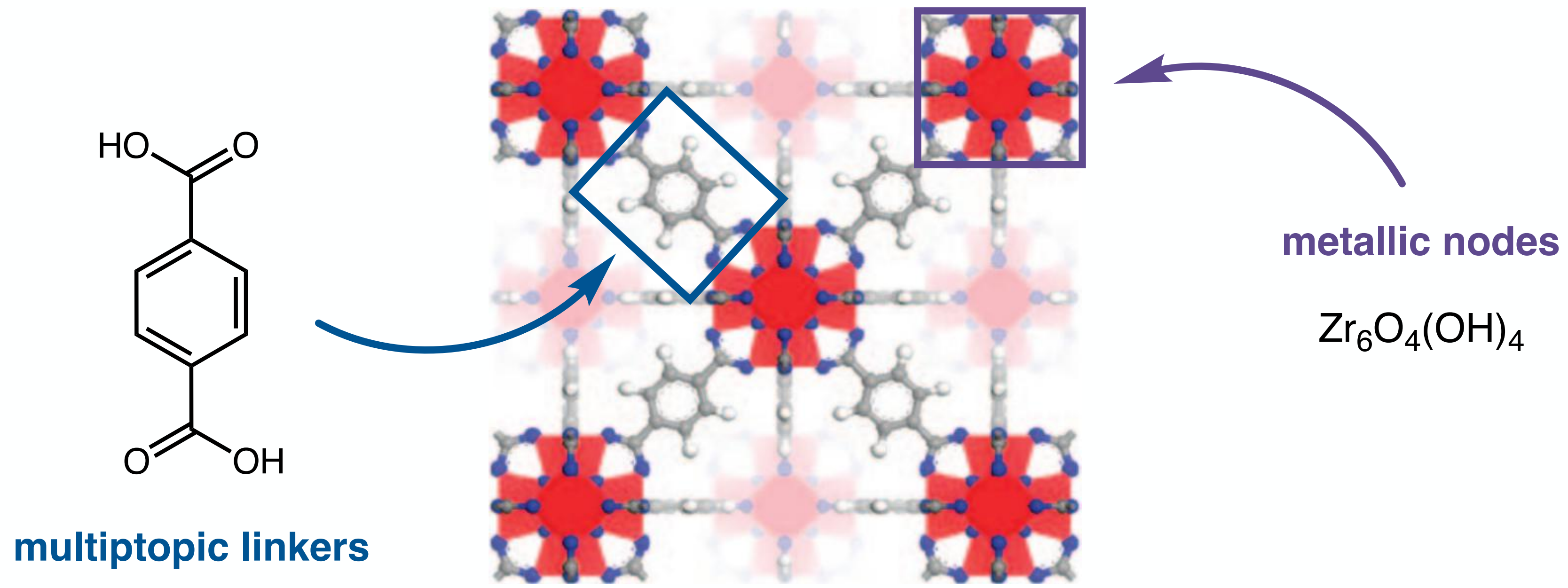
Marissa Lavagnino

MacMillan Group Meeting

25 April 2019

What are Metal-Organic Frameworks?

Metal-Organic Frameworks (MOFs) *are crystalline, periodic, highly porous (up to 94% empty space) frameworks*



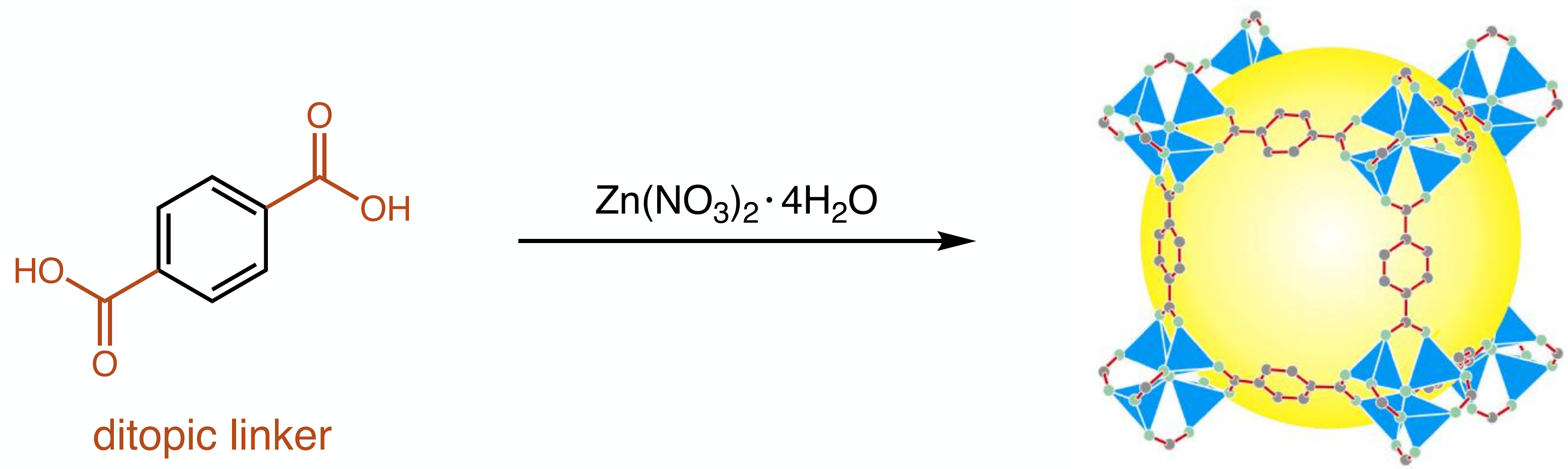
Framework ***self-assemble*** *to form* ***coordination bonds*** *between*

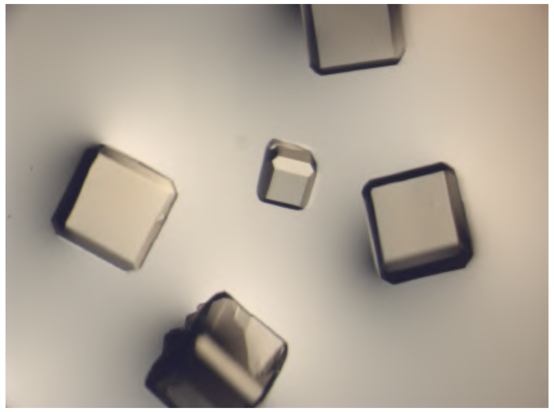
transition metal cations and carboxylate anions

Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012***, 112*, 673-674.

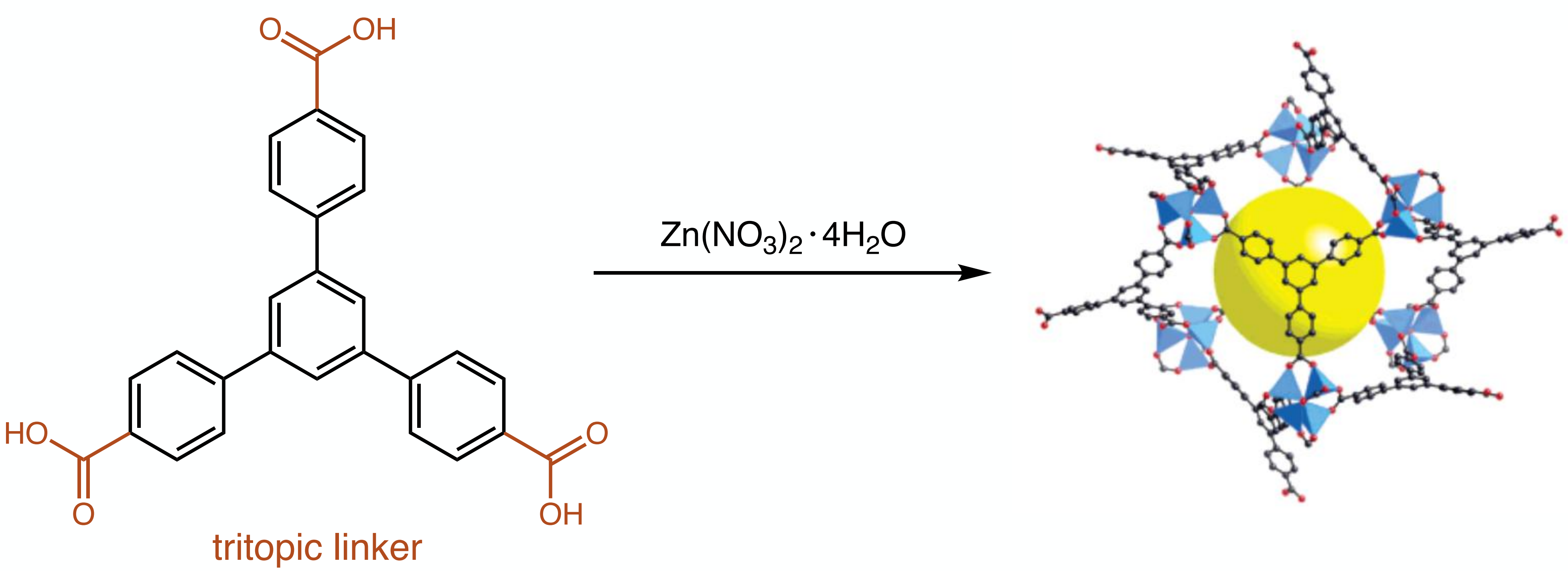
Examples of MOF Structures

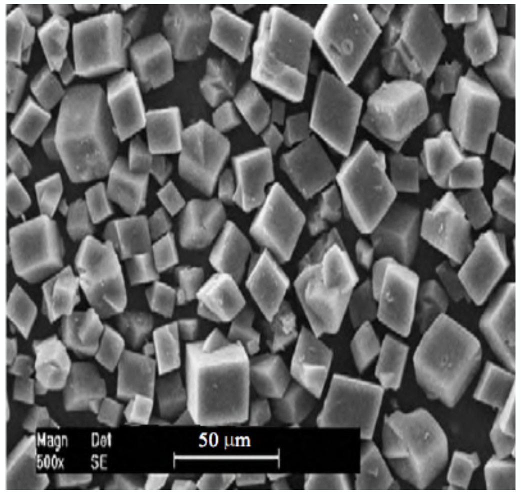
MOF-5





MOF-177



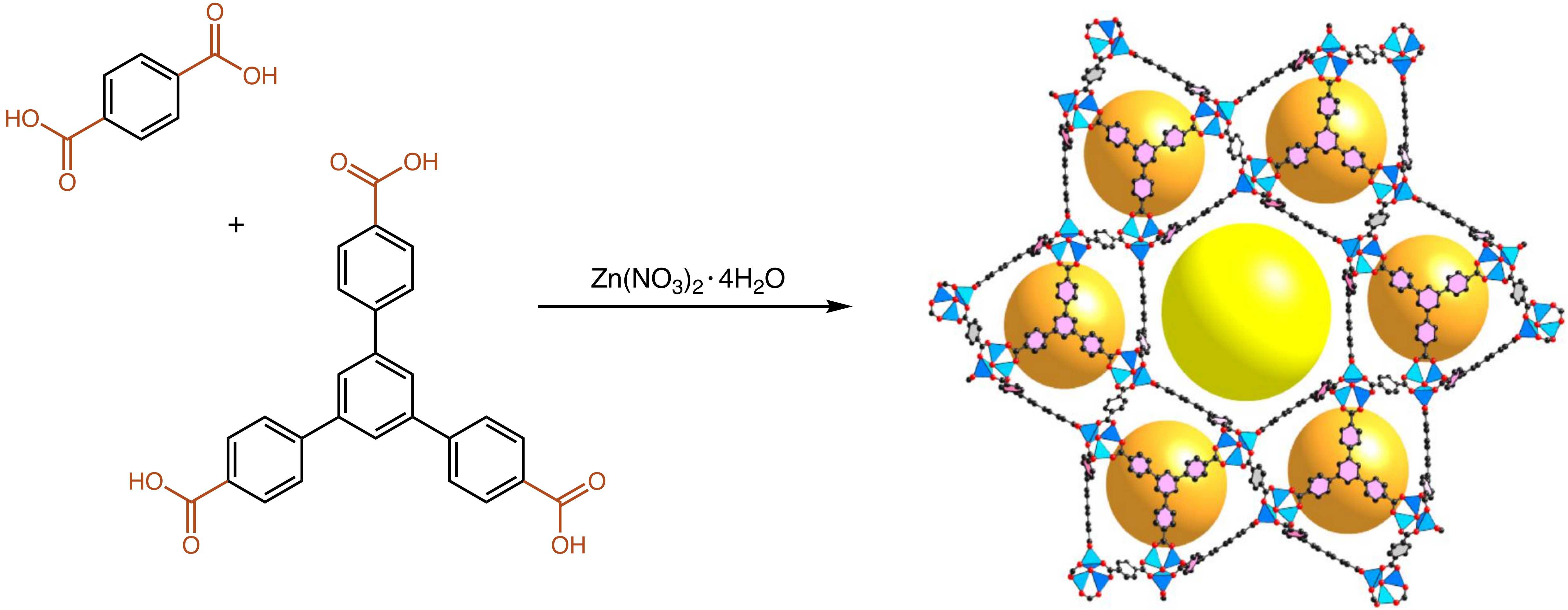


Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.

Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523-527.

Example of a Mixed-Linker MOF Structure

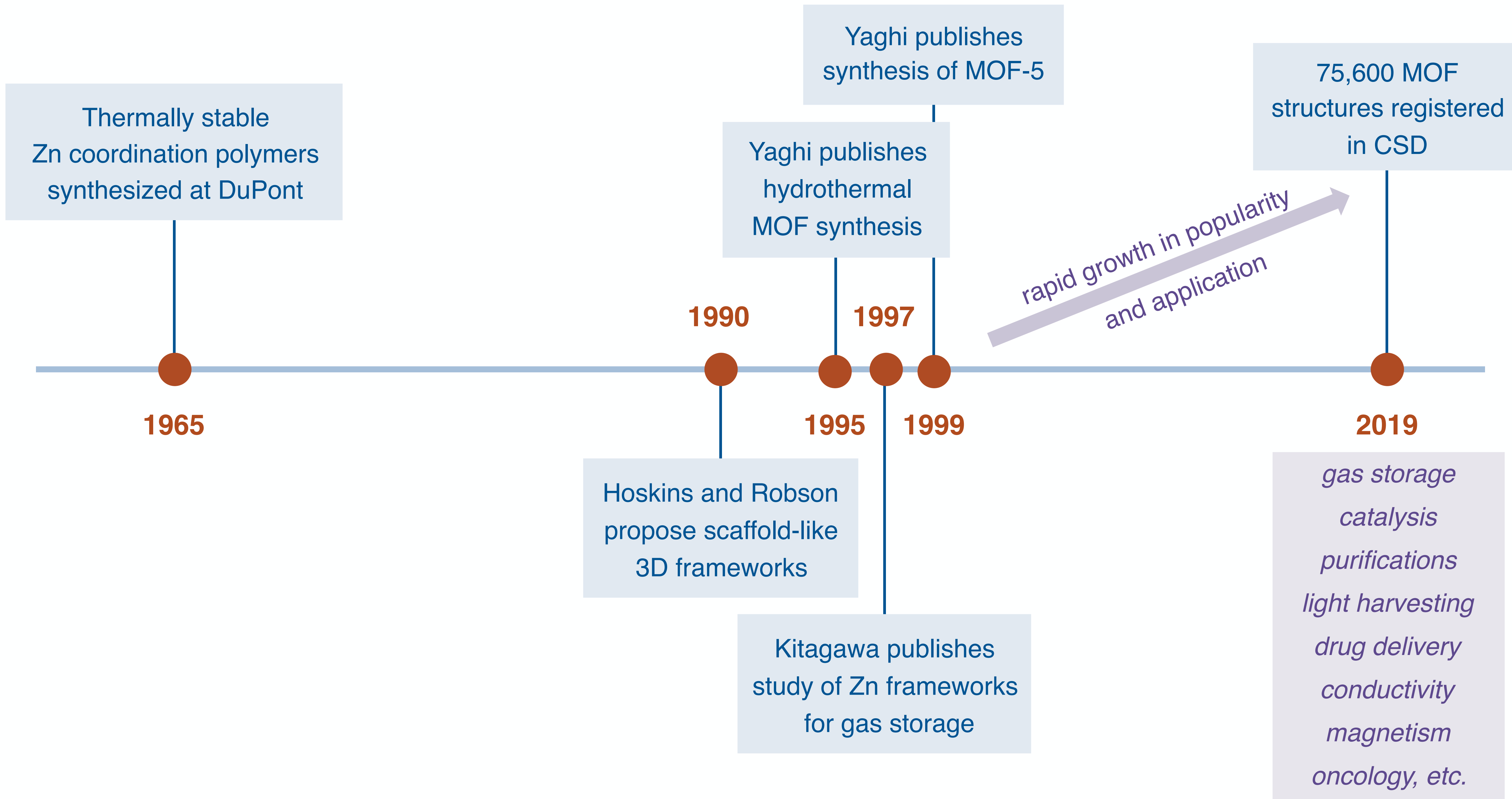
UMCM-1



Due to the modularity of MOF design, a nearly infinite number of topographies can be imagined.

Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 677-680.

A Brief History of Metal-Organic Frameworks



Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

A Roadmap for Metal-Organic Framework Synthesis

Synthesis *through self-assembly*

Activation *by removal of solvent*

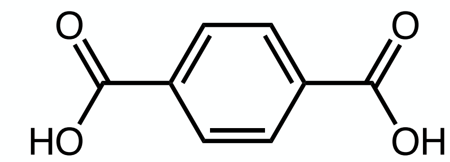
Characterization *to assess purity and crystallinity*

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2017**, *29*, 26-39.

The Conventional Route: Solvothermal Synthesis

$ZnCl_4$

simple metal salt

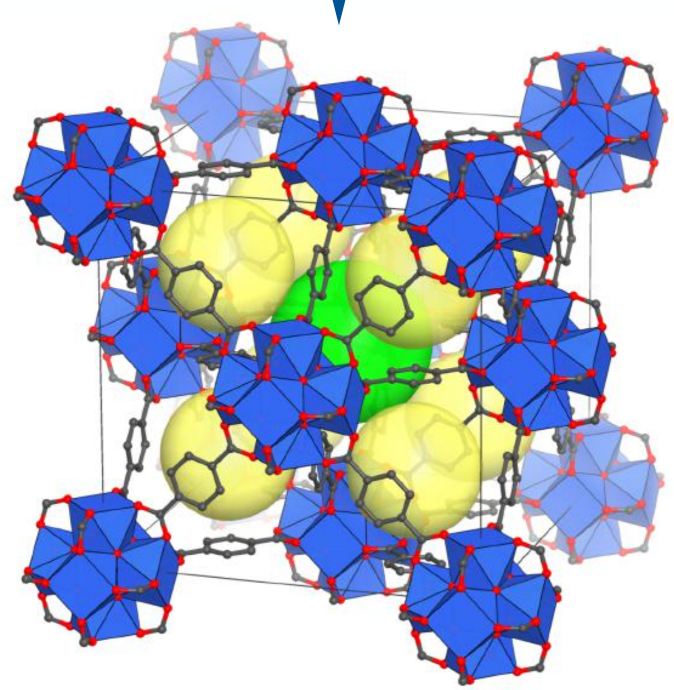


organic linker

1. sonciate in high boiling solvent (e.g. DMF)

2. heat without stirring for hours/days

3. centrifuge and filter



Optimization:

few reaction variables to *manipulate*

temperature

order of addition

metal source

Reproducibility:

many environmental factors to *control*

humidity

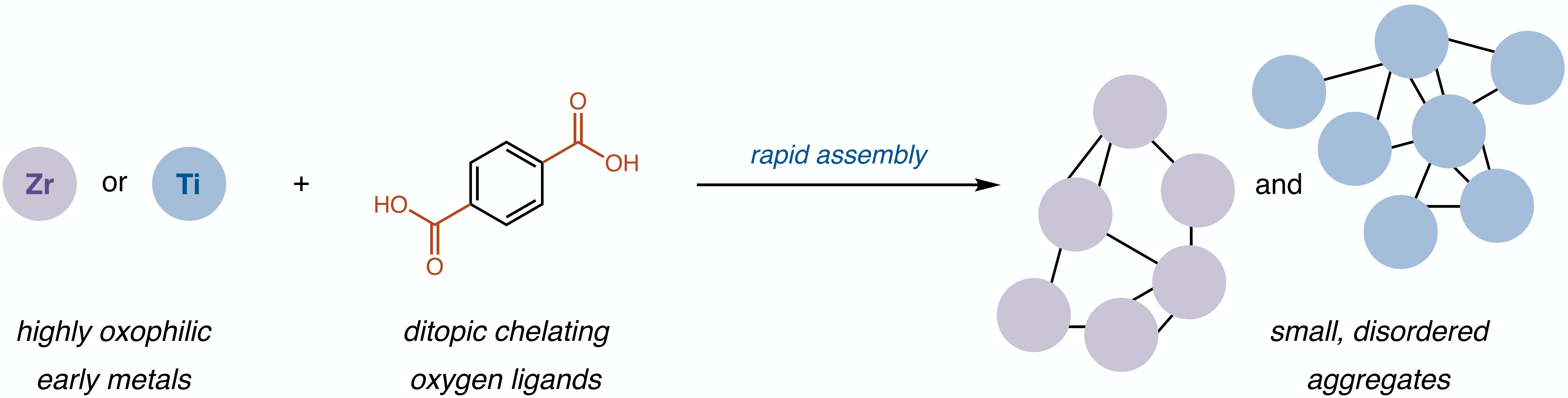
suspension quality

purity of metal salt

speed of assembly

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2017**, *29*, 26-39.

Pitfalls of Uncontrolled Self-Assembly



How do we slow down self-assembly and control lattice quality?

Modulators promote order in MOF self-assembly

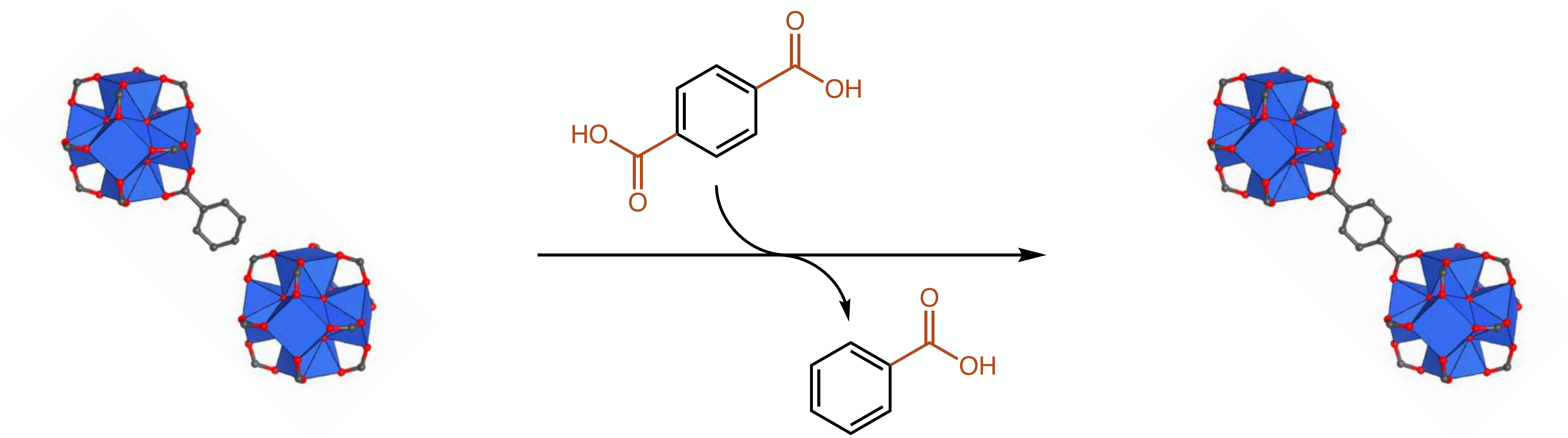
Modulators as Small Molecule Regulators of MOF Growth

Mechanisms of Action

1. Reversibly occupying coordination sites on metal clusters

2. Accelerating metal cluster formation

Case 1: Benzoic and acetic acids



Monotopic coordination to metal clusters slows nucleation rate

Promotes ideal framework assembly

Shaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. *Chem. Eur. J.* **2011**, *17*, 6643-6651.

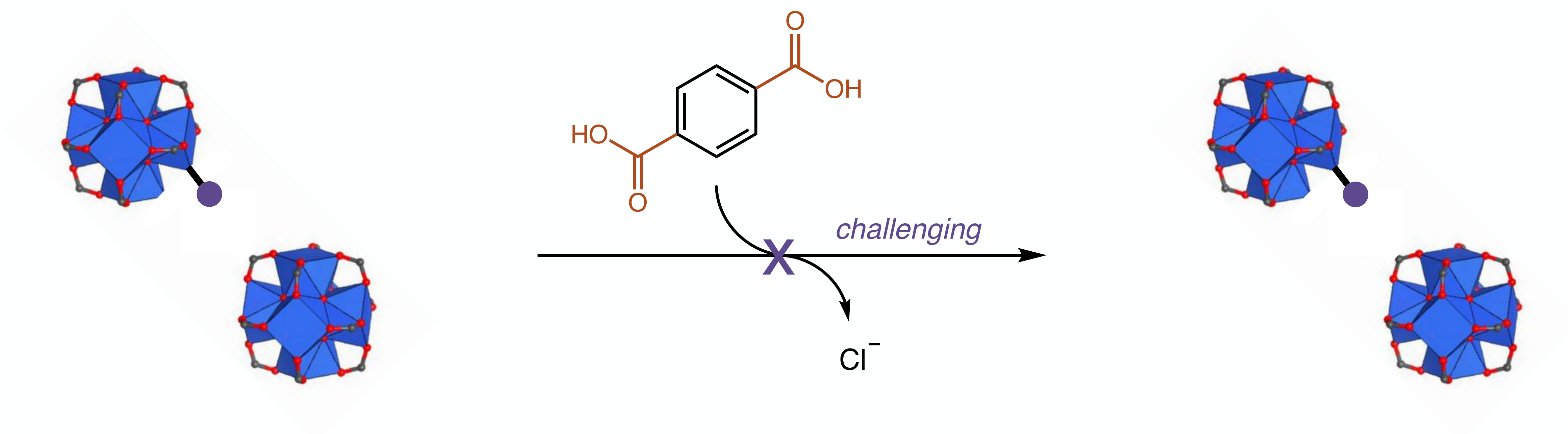
Modulators as Small Molecule Regulators of MOF Growth

Mechanisms of Action

1. Reversibly occupying coordination sites on metal clusters

2. Accelerating metal cluster formation

Case 2: Hydrochloric Acid



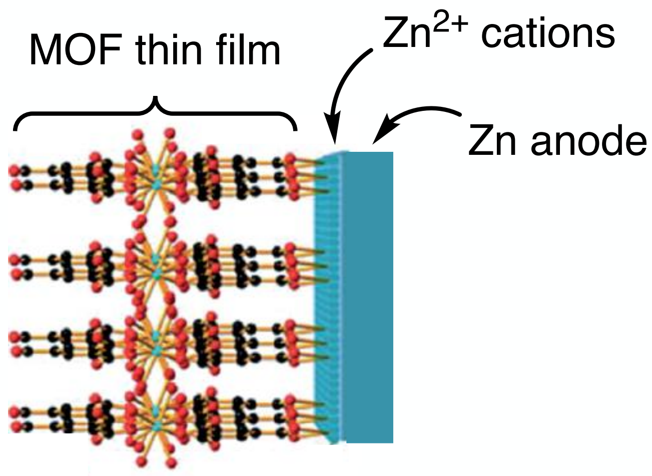
Neutralizes solvent (DMF) and promotes metal cluster formation

Creates missing linker defect sites
(not necessarily a bad outcome)

Katz, M. J.; Brown, Z. J.; Colon, Y, J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2013**, *49*, 9449-9451.

Alternatives to Solvothermal MOF Synthesis

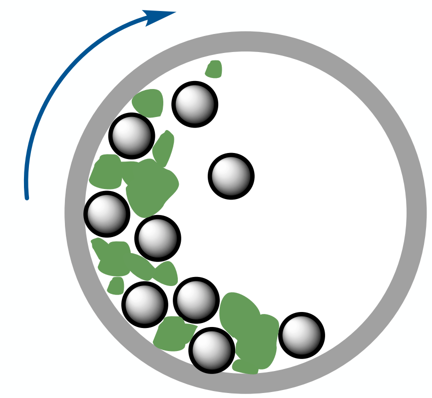
Electrochemical



- metal cations generated on electrode
- application to membranes, sensors, electronics

ChemElectroChem **2015**, *2*, 462-474.

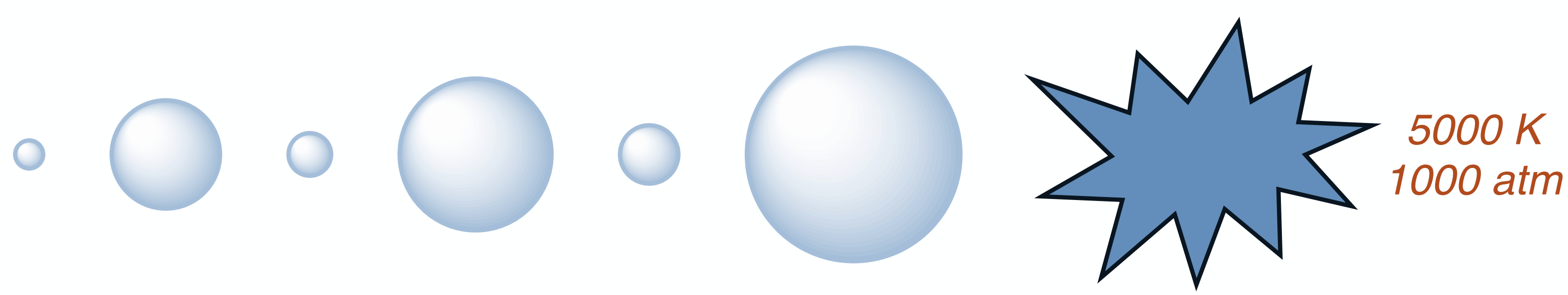
Mechanochemical



- minimal solvent simplifies activation steps
- green synthesis, larger scales, control size

Chem. Mater. **2010**, *22*, 5216-5221.

Sonochemical and Microwave-Assisted



- rapid superheating dissolves metal salts and linkers evenly in solution
- reproducible MOF synthesis

Coord. Chem. Rev. **2015**, *285*, 11-23.

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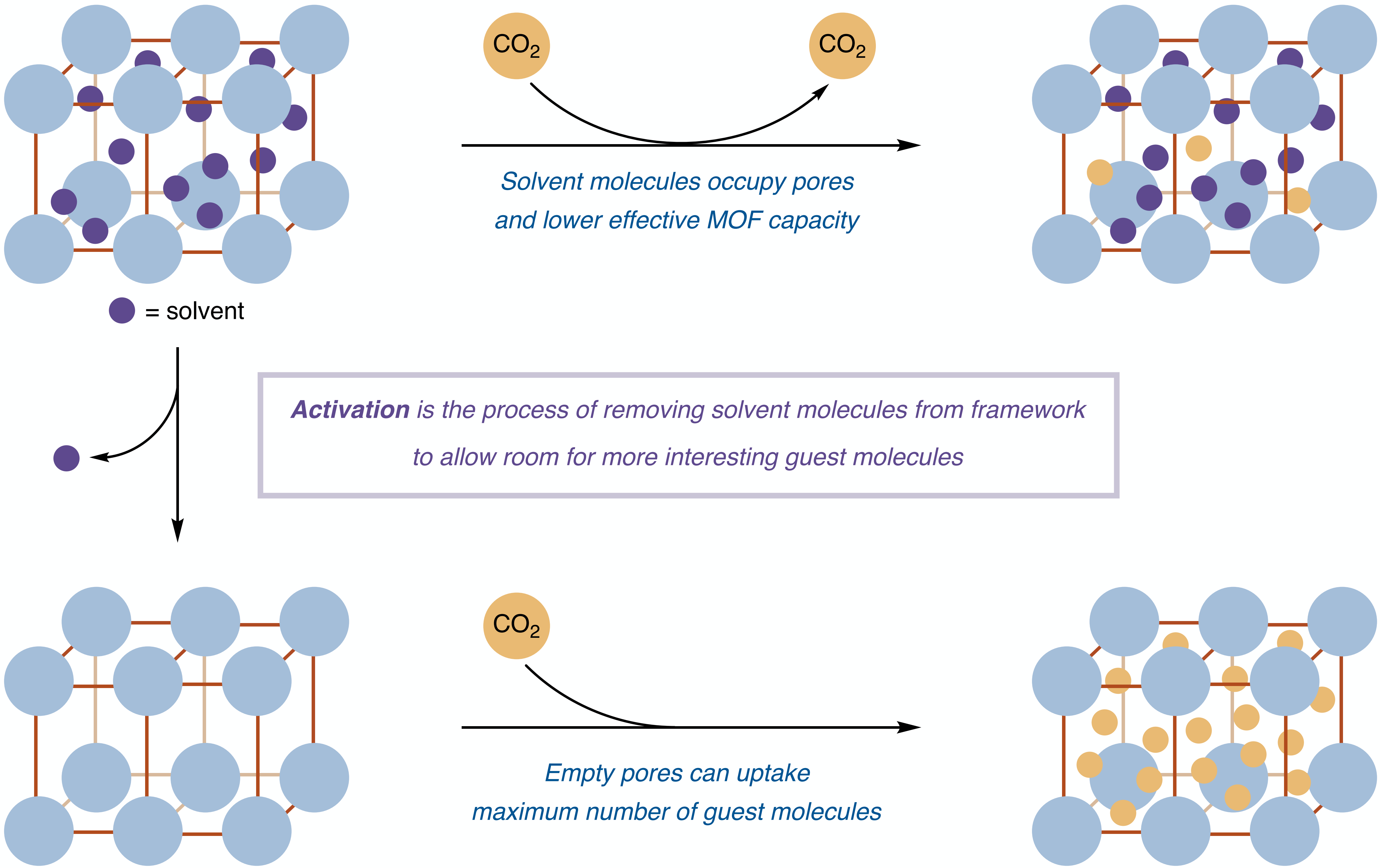
Activation as the Key to Unlocking a MOF's Potential



Katz, M. J.; Brown, Z. J.; Colon, Y, J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2013**, *49*, 9449-9451.

MOF Activation and Solvent Exchange

Activation can be performed by simply heating and applying vacuum

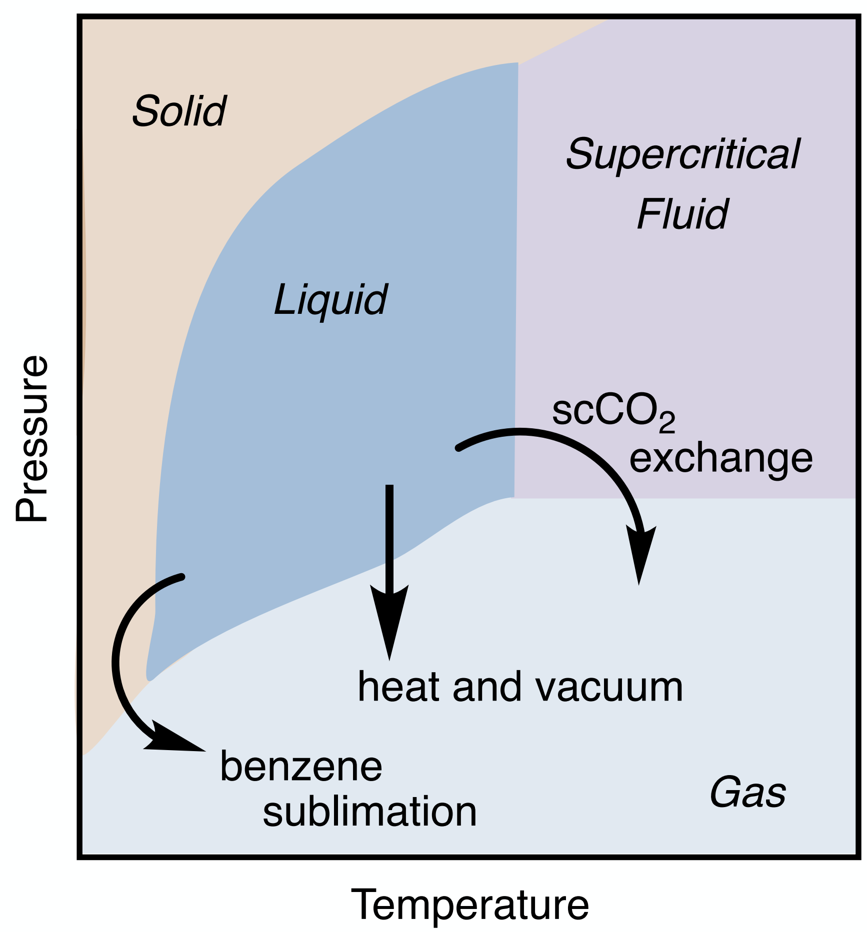
Removing high boiling, high surface tension solvents (like DMF and DMSO)

*can cause **framework collapse** due to capillary forces*

Alternative Strategy #1

Soak MOF in lower boiling solvent

then heat under vacuum



Alternative Strategy #2

Avoid the liquid-gas phase transition

- "green" activation method
- easily scalable

Mondloch, J. E.; Karagiaridi, O.; Farha, O. K.; Hupp, J. T. *CrystEngComm* **2013**, *15*, 9258-9264.

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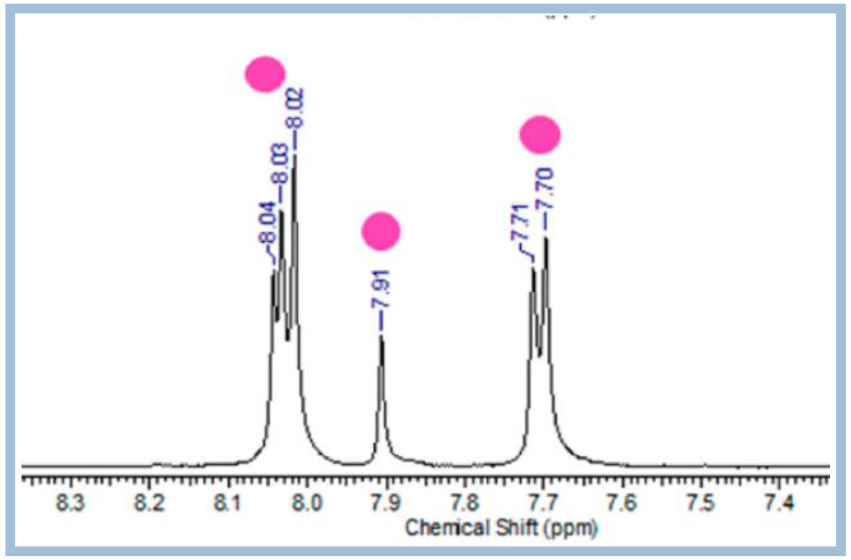
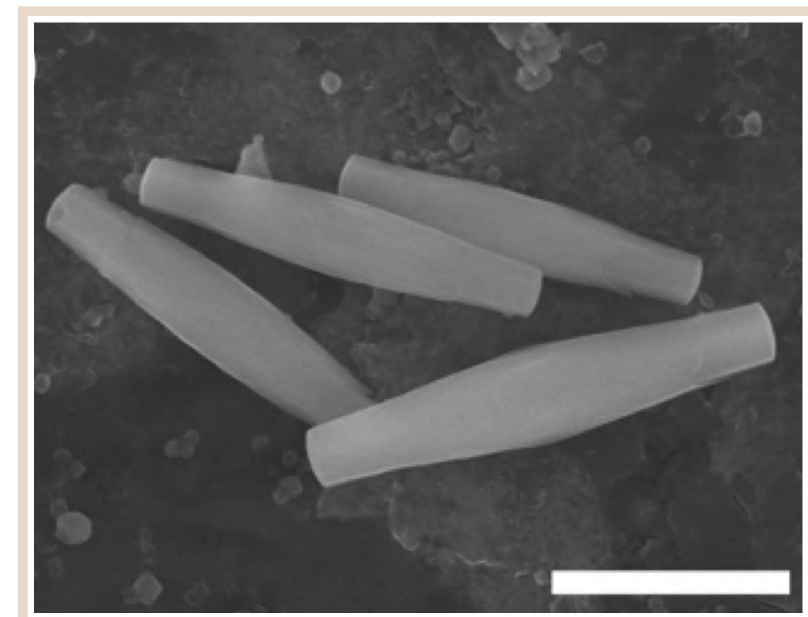
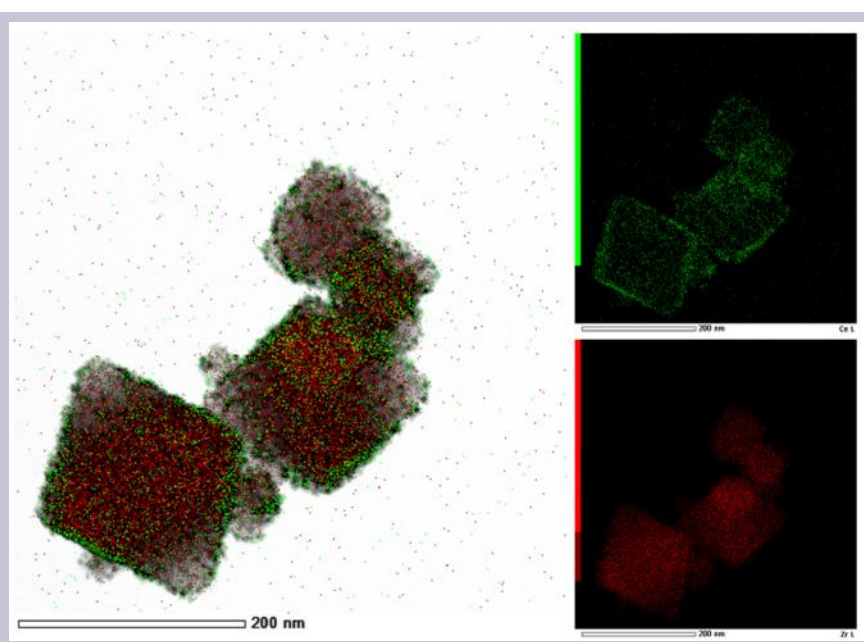
MOF Characterization Techniques



^{1}H NMR Spectroscopy *assays the bulk purity of the sample by quantifying the relative amounts of incorporated and free organic linker*



Scanning Electron Microscopy (SEM) *allows the chemist to observe crystal size, morphology, and uniformity*

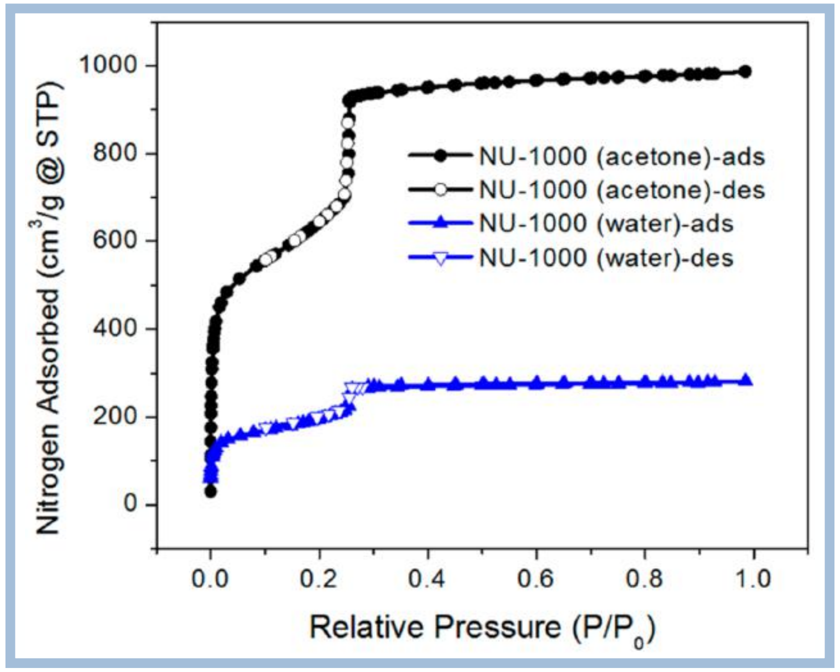


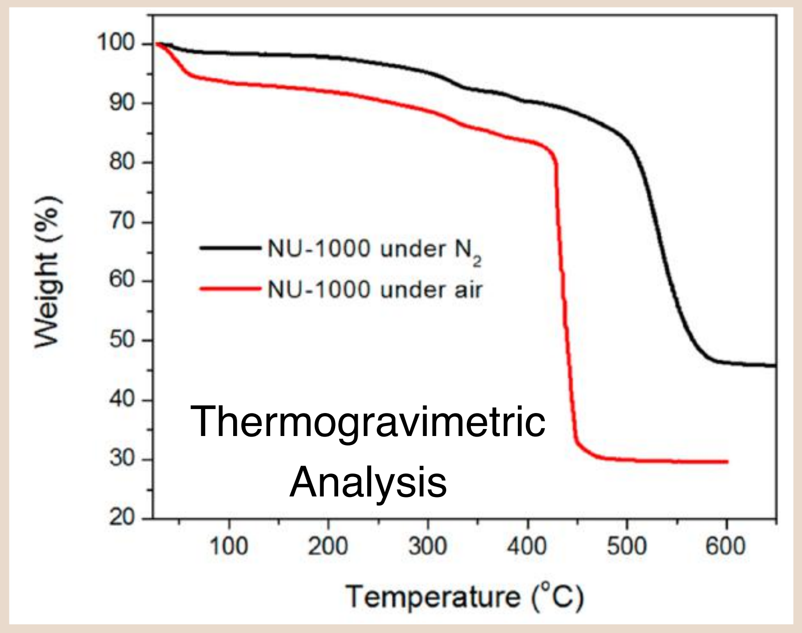
SEM *in conjunction with* ***Electron Diffraction X-Ray (EDX) Spectroscopy*** *maps the elemental composition throughout the framework*

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2017**, *29*, 26-39.

MOF Characterization Techniques

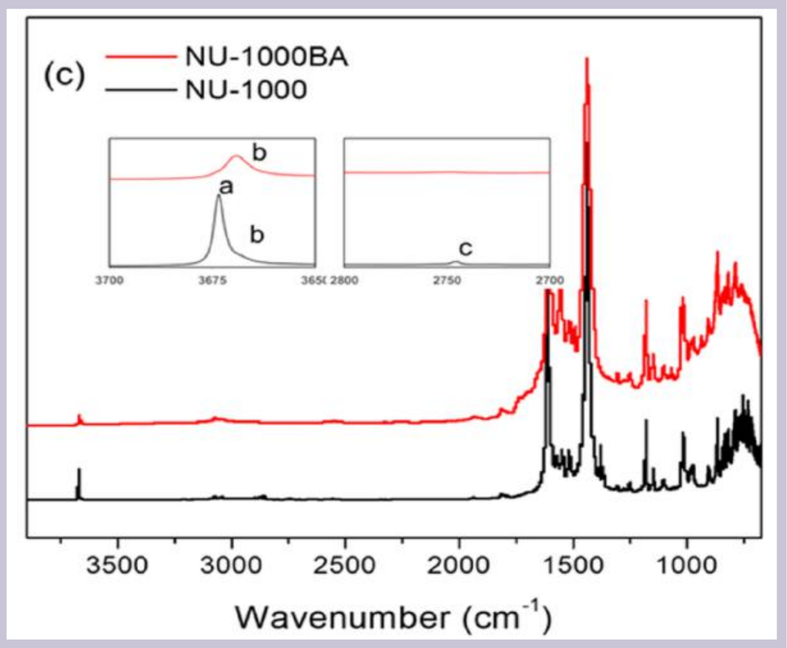
***N_2 Adsorption/Desorption Isotherms** measure the apparent surface area of the MOF (i.e., the capacity of the MOF to store guest molecules)*





***Stability tests** assess the framework under relevant conditions (e.g.; aqueous, pH, photochemical, and **thermal stability**)*

***Diffuse Reflectance Infared Fourier Transform Specroscopy (DRIFTS)** can show the interaction of the framework with guest molecules*



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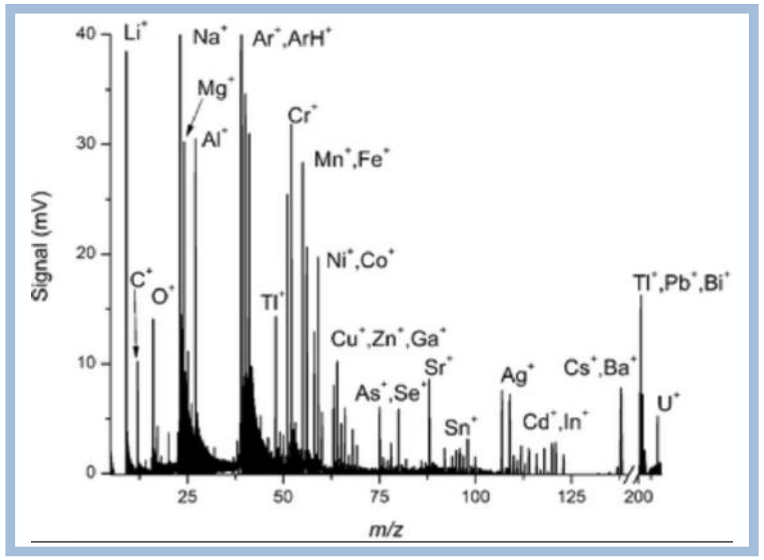
MOF Characterization Techniques

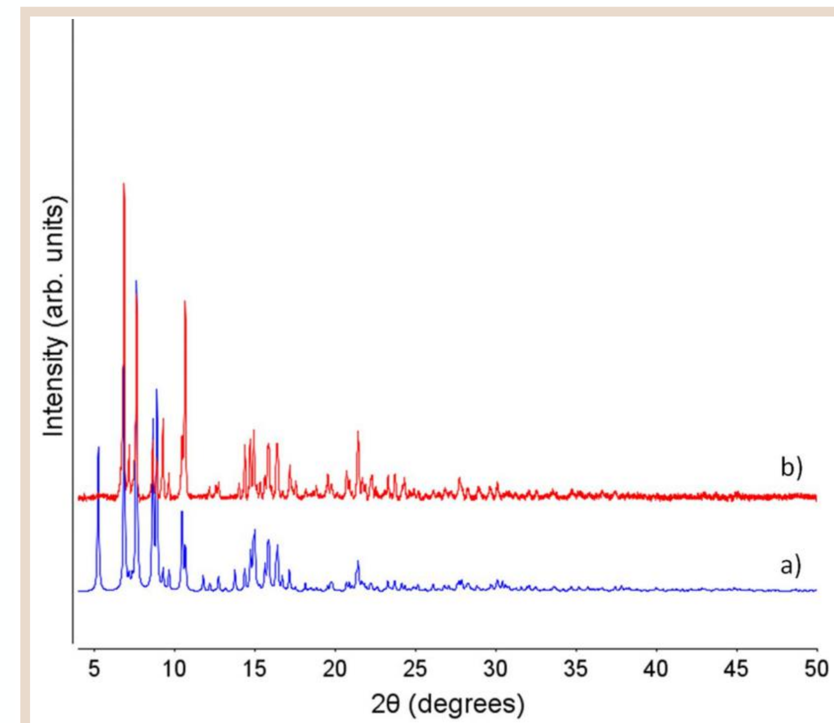


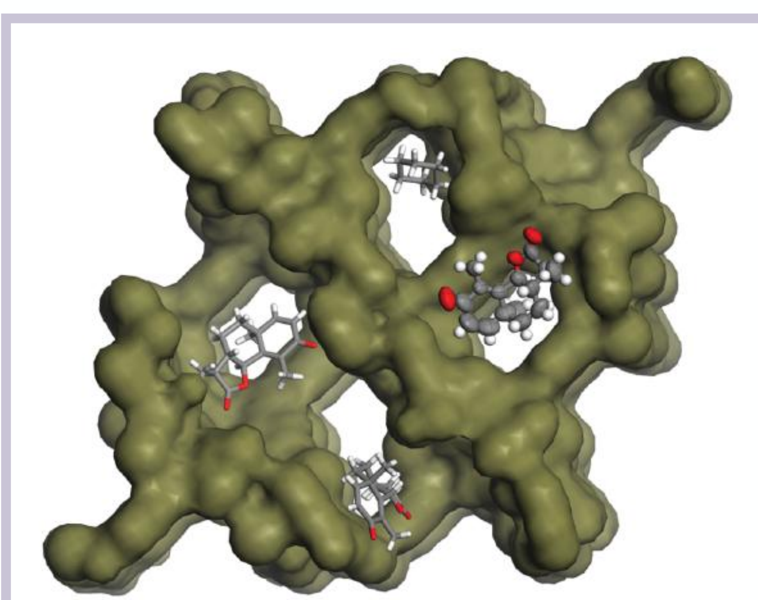
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

*and **Mass Spectroscopy (ICP-MS)** can confirm elemental ratios at ppb or ppt levels*

***Powder X-Ray Diffraction (PXRD)** confirms bulk crystallinity*

of the sample and unit cell size can also be extrapolated





***Single Crystal X-Ray Diffraction** gives absolute structural information*

but is limited by the ability to grow single crystals of sufficient size (5-10 μm)

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2017**, *29*, 26-39.

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Catalysis in Metal-Organic Frameworks

unique steric environment

site-isolation protects catalysts

access reactivities and selectivities not seen in solution

Pascanu, V.; González Miera, G.; Inge, A. K.; Martín-Matute, B. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

Biomimetic Catalysis

Asymmetric Catalysis

Organocatalysis

Catalysis in Metal-Organic Frameworks

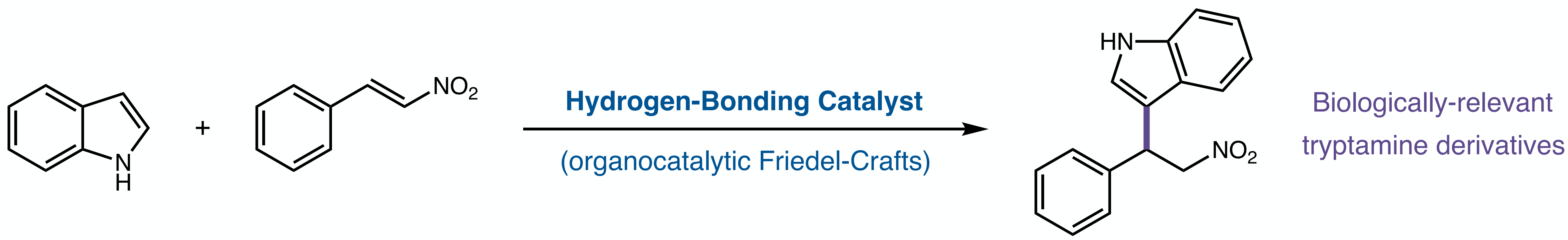
Olefin Metathesis

Photocatalysis and Metallaphotoredox

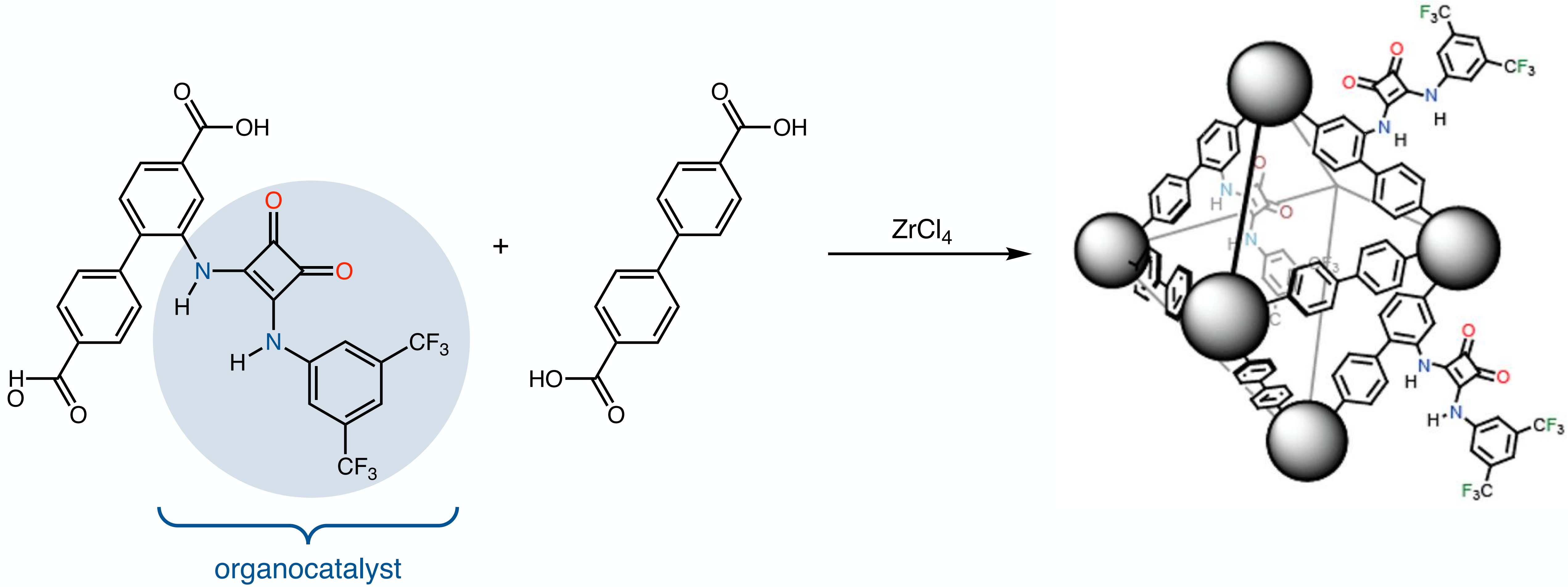
Mechanistic Study

Pascanu, V.; González Miera, G.; Inge, A. K.; Martín-Matute, B. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

“Turning on” a Novel Organocatalyst through Site Isolation

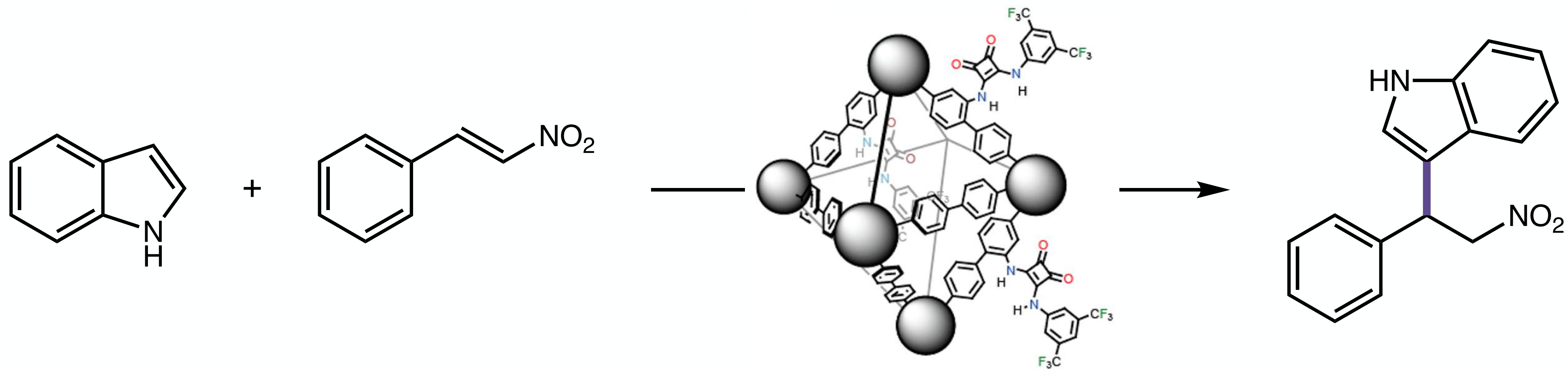


mixed-linker MOF organocatalyst synthesis



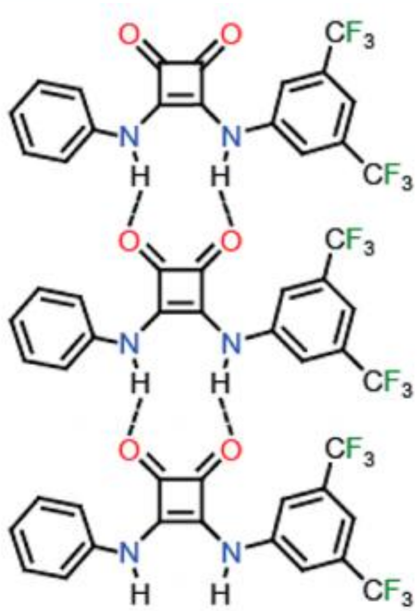
McGuirk, C. M.; Katz, M. J.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. M.; Mirkin, C. A. *J. Am. Chem. Soc.* **2015**, *137*, 919-925.

"Turning on" a Novel Organocatalyst in MOF



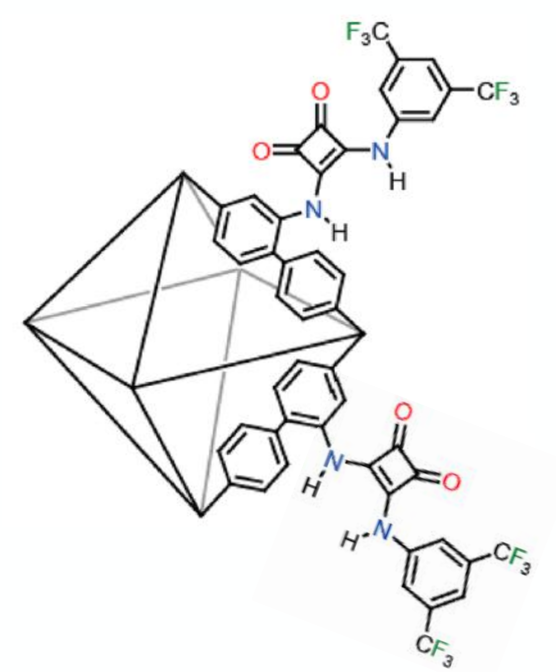
93% yield over 24h
at 50 °C in 1,2-DCB

Unbound squaramide



low yield (7%) attributed to
self-association in solution

Ratio of functionalized:unfunctionalized linker



diminished pore volume
prevents substrate diffusion
(22% yield)

Possible to design and use organocatalysts that would be inactive in solution

McGuirk, C. M.; Katz, M. J.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. M.; Mirkin, C. A. *J. Am. Chem. Soc.* **2015**, *137*, 919-925.

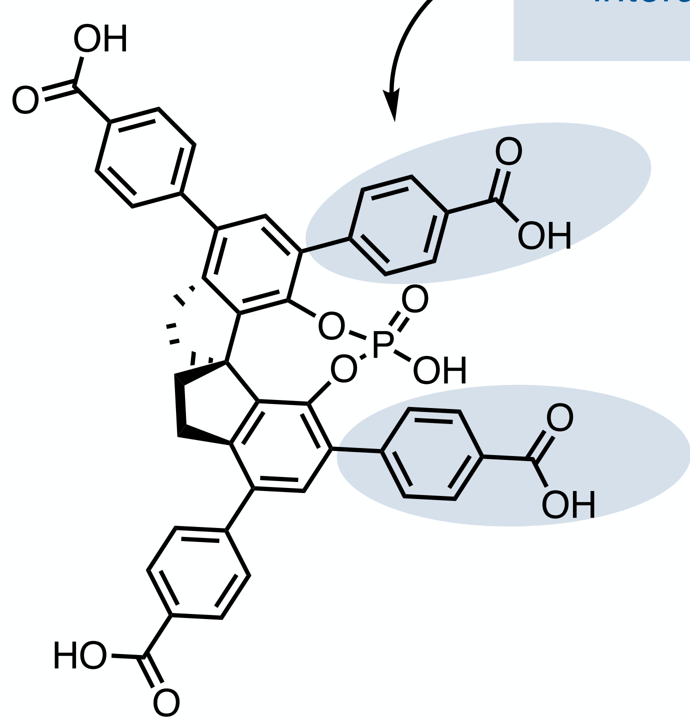
Chiral MOF Catalysis

MOFs constructed from chiral organic linkers can be used in enantioselecgive organic transformations

Chiral pore environment reinforces enantioselectivity of chiral phosphoric acid

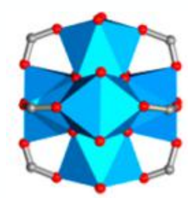
protects phosphate from interaction with Zr(IV)

Periodic lattice ensures identical active site throughout material (vs. other solid supports)

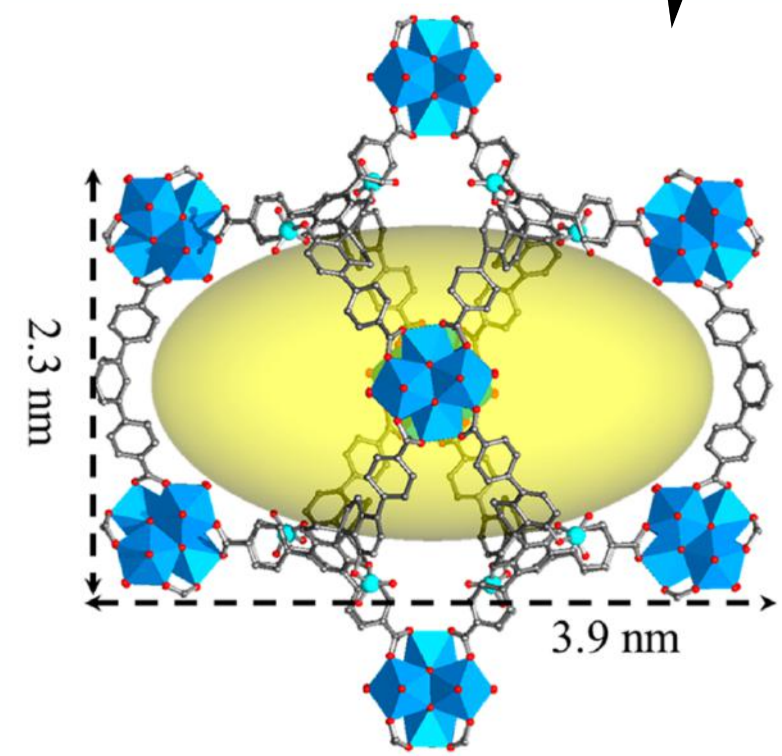


(*S*)-Tetratopic Linker-1

(2.8 ≤ H_0 ≤ 3.3)



$Zr_6O_4(OH)_8(H_2O)_4(COO)_8$



(*S*)-Spiro-1

(-3.0 ≤ H_0 ≤ -2.4)

Lewis acid coordination increases Brønsted acidity

Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

Chiral MOF Catalysis

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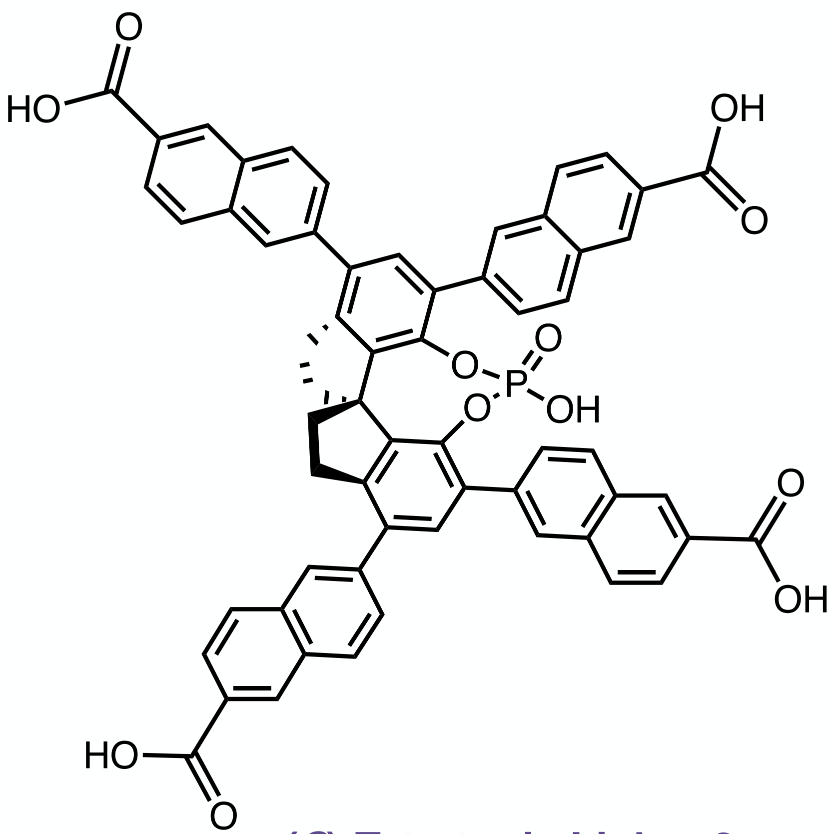
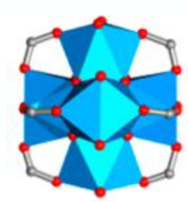


(*S*)-Tetratopic Linker-2

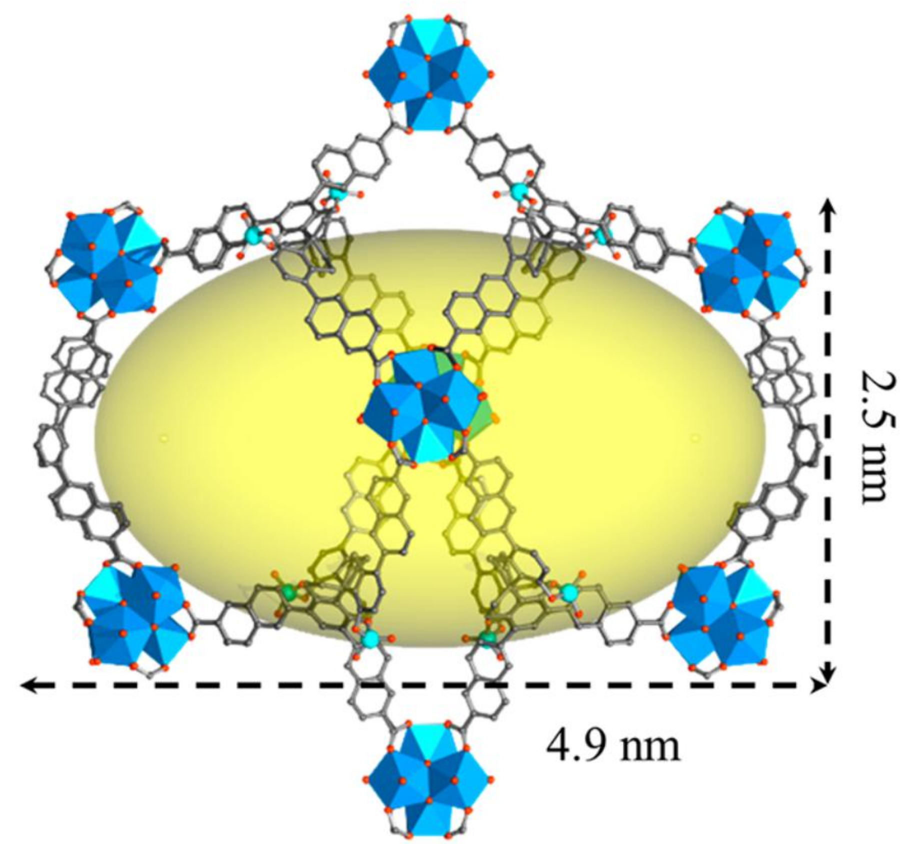
($2.8 \leq H_0 \leq 3.3$)



$Zr_6O_4(OH)_8(H_2O)_4(COO)_8$

MOF synthesis is amenable

to variable linker lengths



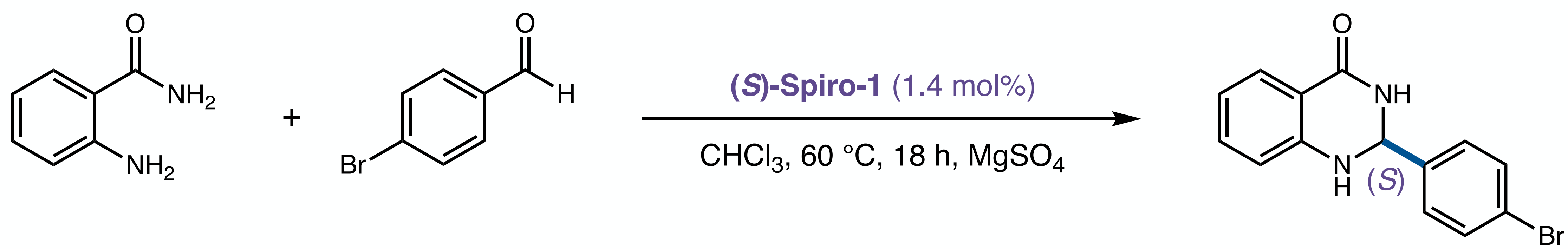
(*S*)-Spiro-2

($-2.4 \leq H_0 \leq -0.2$)

Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

MOF Structure Contributes to Enantioselectivity

Condensation-Cyclization of 2-Aminobenamides and Aldehydes



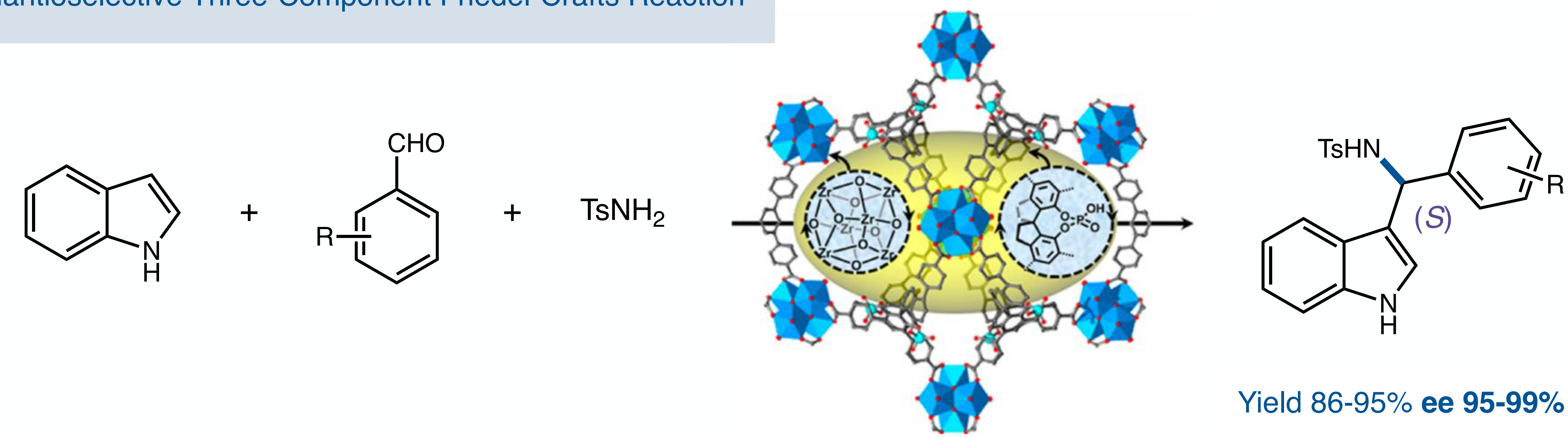
Catalyst	product yield (%)	product stereochemistry	product ee (%)
(*S*)-Spiro-1	99	(*S*)	96
(*R*)-Spiro-1	99	**(*R*)**	96
(*S*)-**free** phosphoric acid	99	(*S*)	**76**
(*S*)-Spiro-**2**	99*	(*S*)	**87**

***faster reaction** due to larger pores, faster substrate diffusion

Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

MOF Functions as a Brønsted Acid and a Lewis Acid

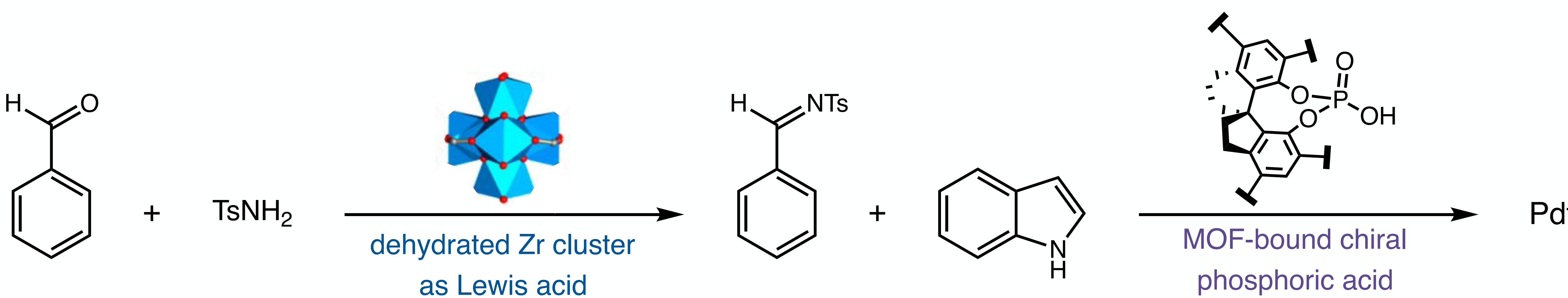
Enantioselective Three-Component Friedel-Crafts Reaction



Yield 86-95% **ee 95-99%**

dehydrated-(*S*)-Spiro-1 (1.4 mol%)

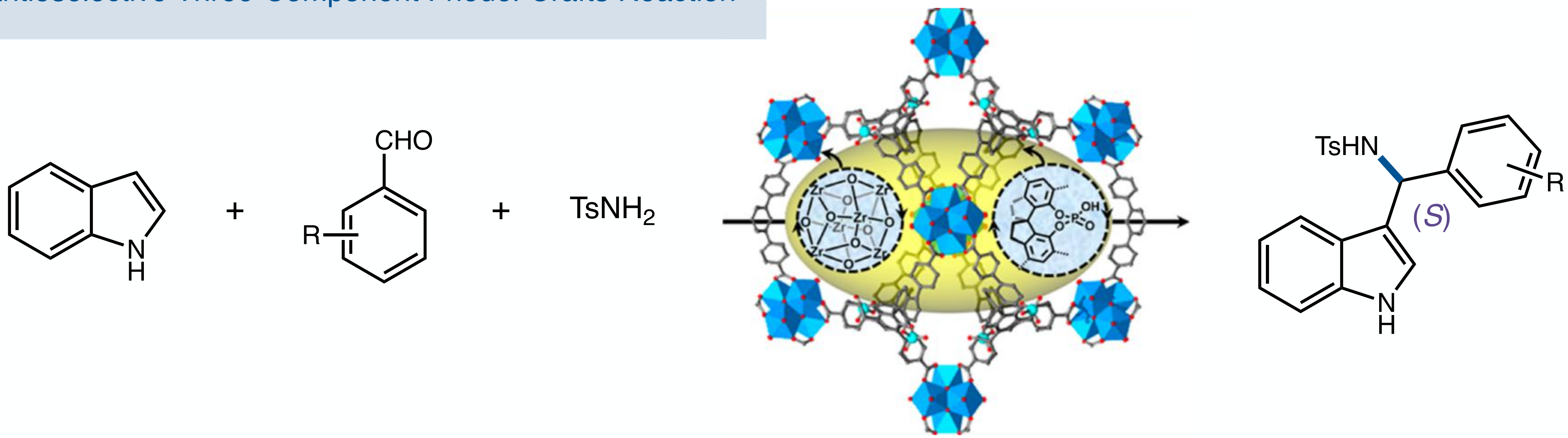
Dual Brønsted and Lewis Acid Catalysis



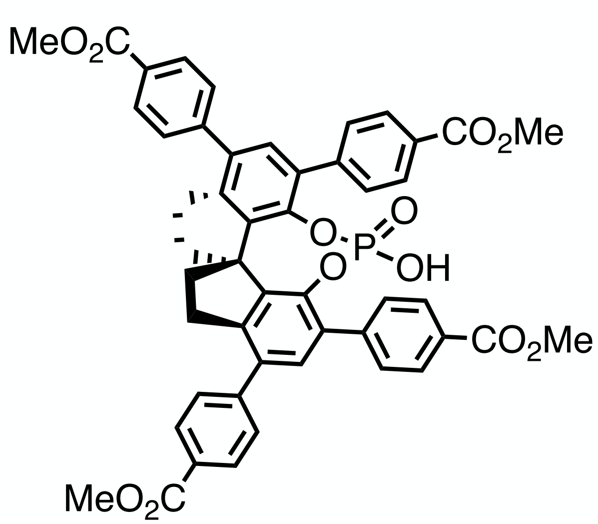
Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

Control Reactions

Enantioselective Three-Component Friedel-Crafts Reaction

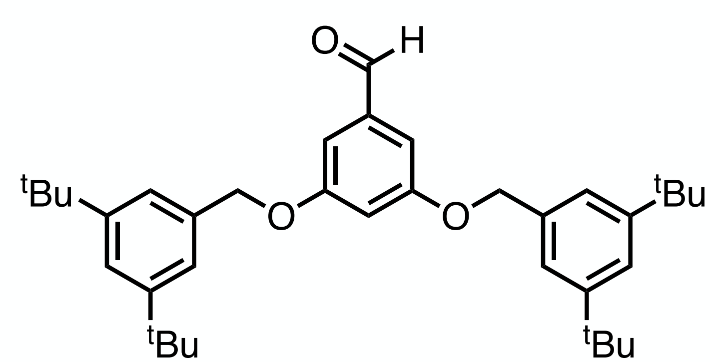


Free phosphoric acid



no reaction,
Lewis acid also required

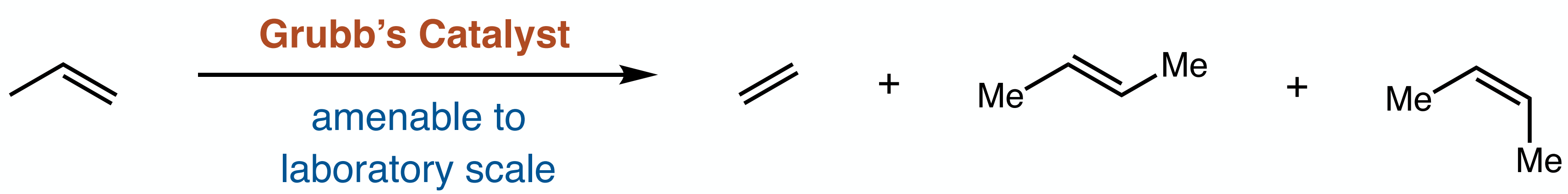
Sterically hindered aldehydes

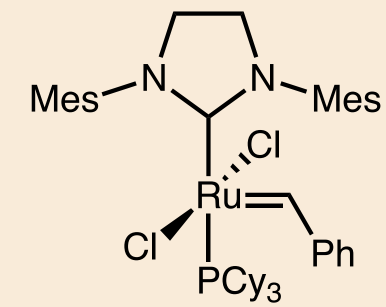


no reaction,
suggests reactivity is in MOF pore

Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. *J. Am. Chem. Soc.* **2019**, *ASAPs*.

Activation of an Olefin Metathesis Catalyst by Lewis Acidic Metal Clusters



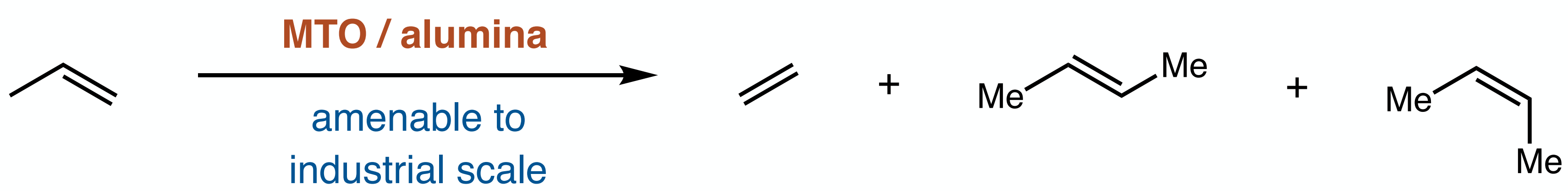


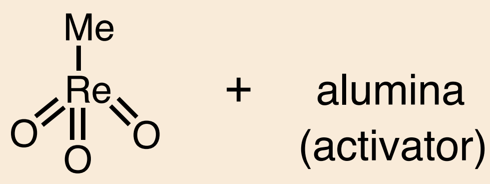
Grubb's Catalyst 2nd Gen

(homogeneous conditions)

Korzynski, M. D.; Consoli, D. F.; Zhang, S.; Roman-Leshkov, Y.; Dinca, M. *J. Am. Chem. Soc.* **2018**, *140*, 6956-6960.

Activation of an Olefin Metathesis Catalyst by Lewis Acidic Metal Clusters





Methyltrioxorhenium (MTO)

(heterogeneous conditions)

Would the metal clusters of a Zr MOF be Lewis acidic enough to activate MTO?

Defined active sites of a single type (unlike other supports)

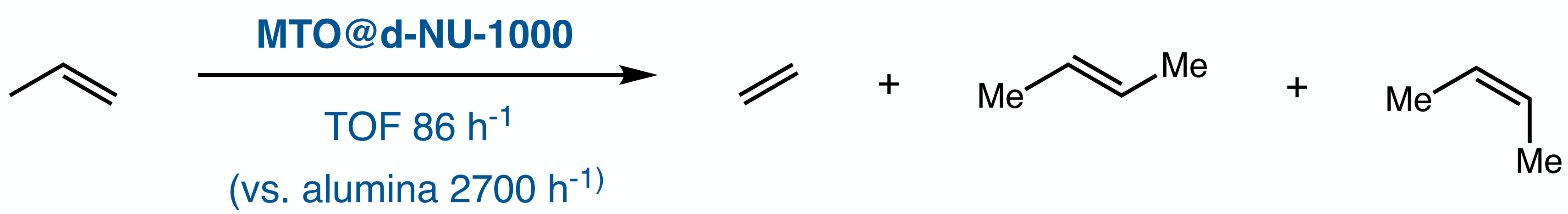
Highly tunable local environment

Possibility of mechanistic study via x-ray diffraction and other spectroscopic tools

Korzynski, M. D.; Consoli, D. F.; Zhang, S.; Roman-Leshkov, Y.; Dinca, M. *J. Am. Chem. Soc.* **2018**, *140*, 6956-6960.

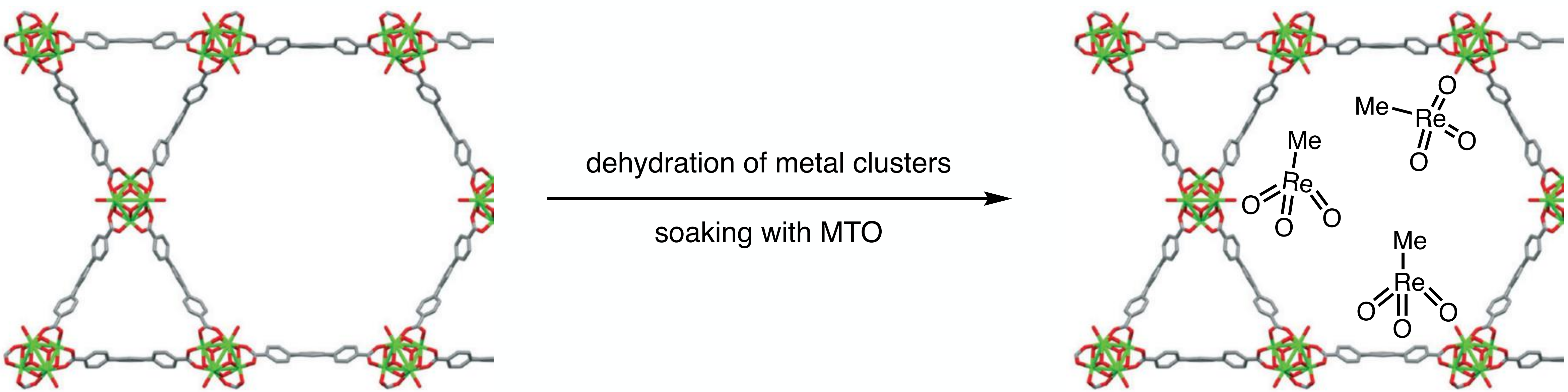
Activation of an Olefin Metathesis Catalyst by Lewis Acidic Metal Clusters

trans:cis = 1:1.3
(consistent with steric effect of MOF)



First activation of MTO by zirconium

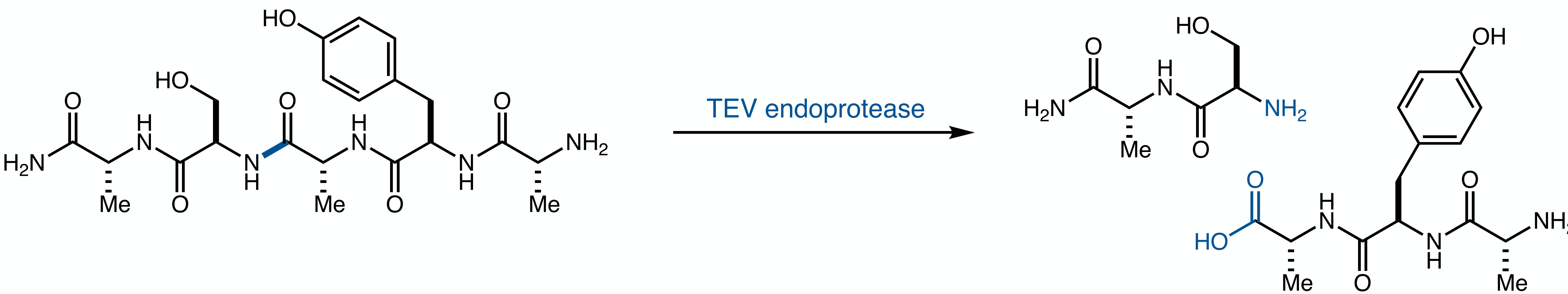
NU-1000 **MTO@d-NU-1000**

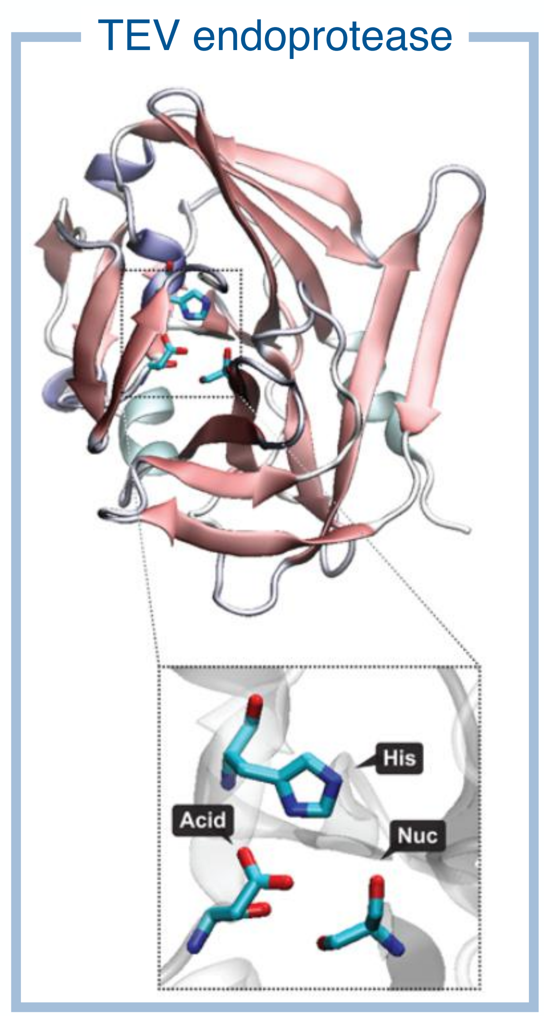


0.5 molecule MTO / Zr cluster

Korzynski, M. D.; Consoli, D. F.; Zhang, S.; Roman-Leshkov, Y.; Dinca, M. *J. Am. Chem. Soc.* **2018**, *140*, 6956-6960.

Enzyme-Like Complexity in a MOF Pore





Recognizes serine in a peptide

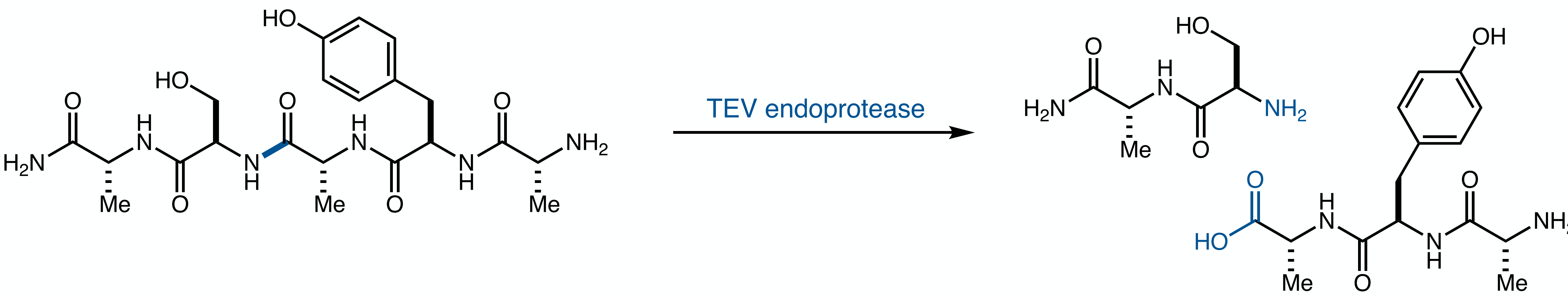
and cleaves the next amide bond

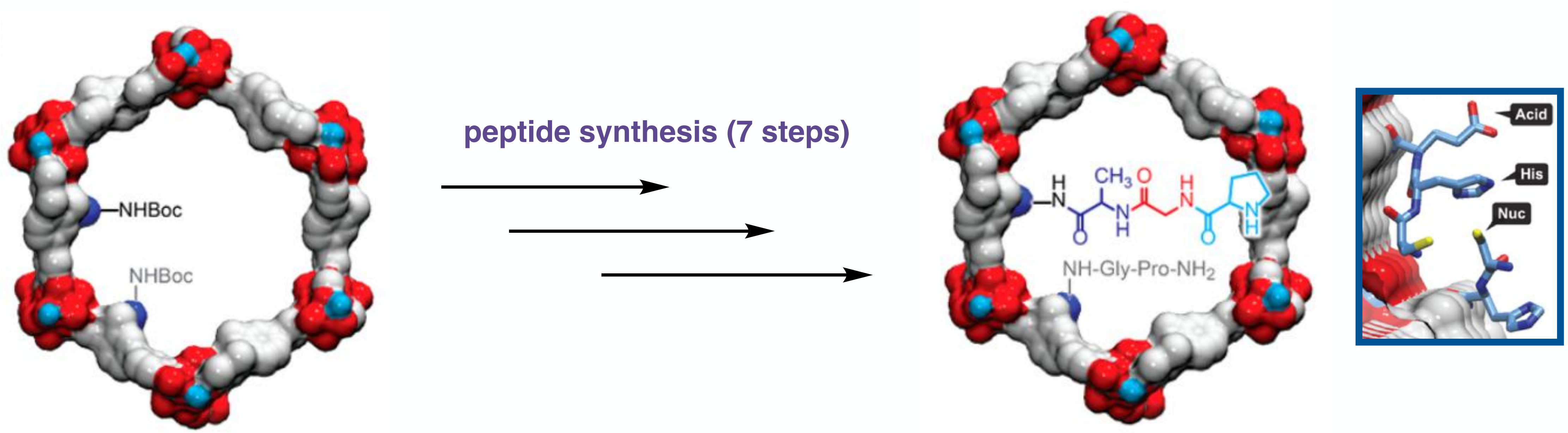
proposed cooperative catalysis between

Asp (Acid), His, and Cys/Ser (Nuc)

Fracaroli, A. M.; Siman, P.; Nagib, D. A.; Suzuki, M.; Furukawa, H.; Toste, F. D.; Yaghi, O. M. *J. Am. Chem. Soc.* **2016**, *138*, 8352-8355.

Enzyme-Like Complexity in a MOF Pore





Results

1. **Selective conversion** to cleaved product was observed (5% over 24 hours)

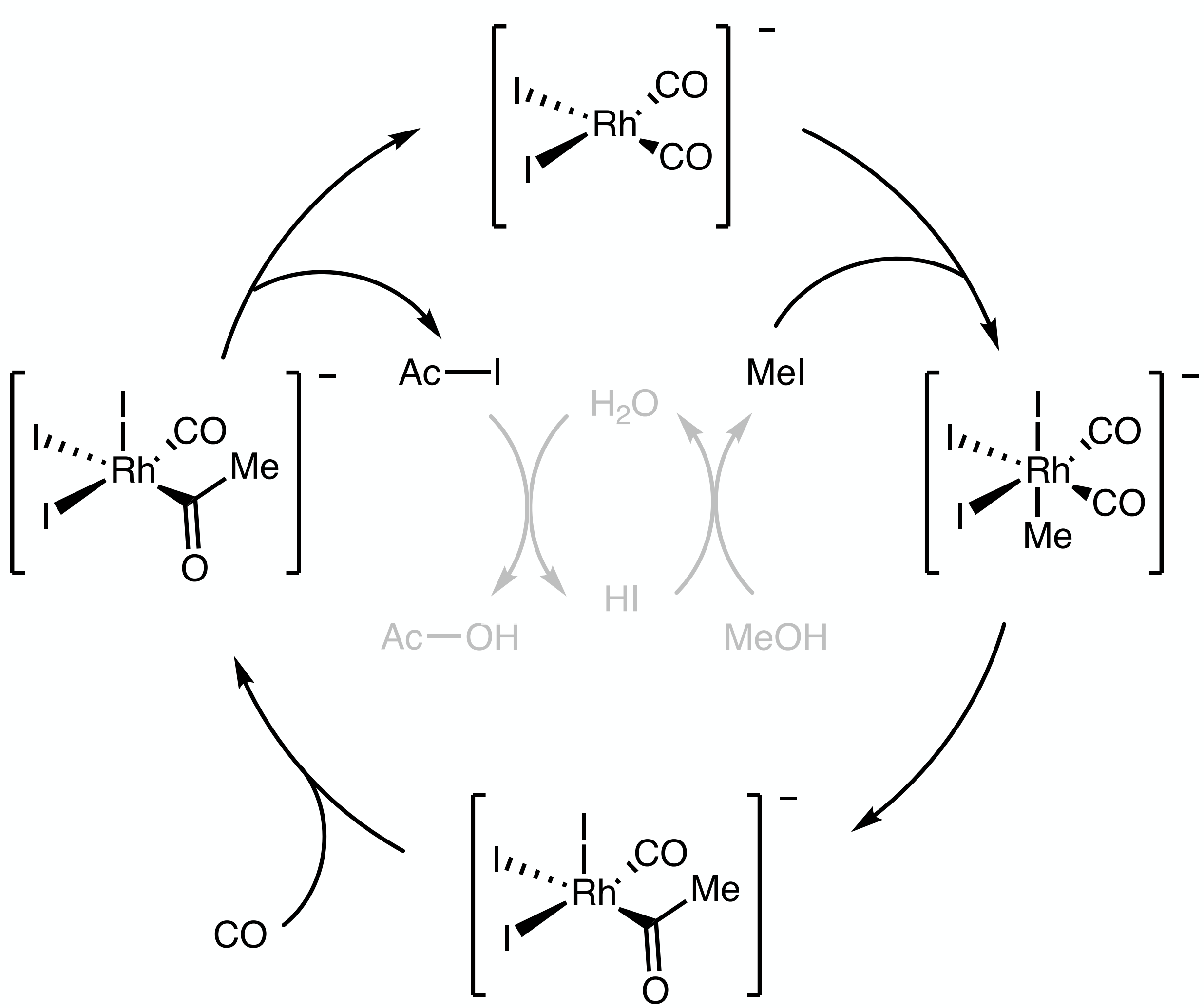
2. Unsupported tripeptide showed **no catalytic activity**

Fracaroli, A. M.; Siman, P.; Nagib, D. A.; Suzuki, M.; Furukawa, H.; Toste, F. D.; Yaghi, O. M. *J. Am. Chem. Soc.* **2016**, *138*, 8352-8355.

Single-Crystal X-Ray Crystallography to Map a Catalytic Process

Crystalline, sterically encumbered MOFs allow for study of catalytically relevant organometallic intermediates

Monsanto Acetic Acid Process

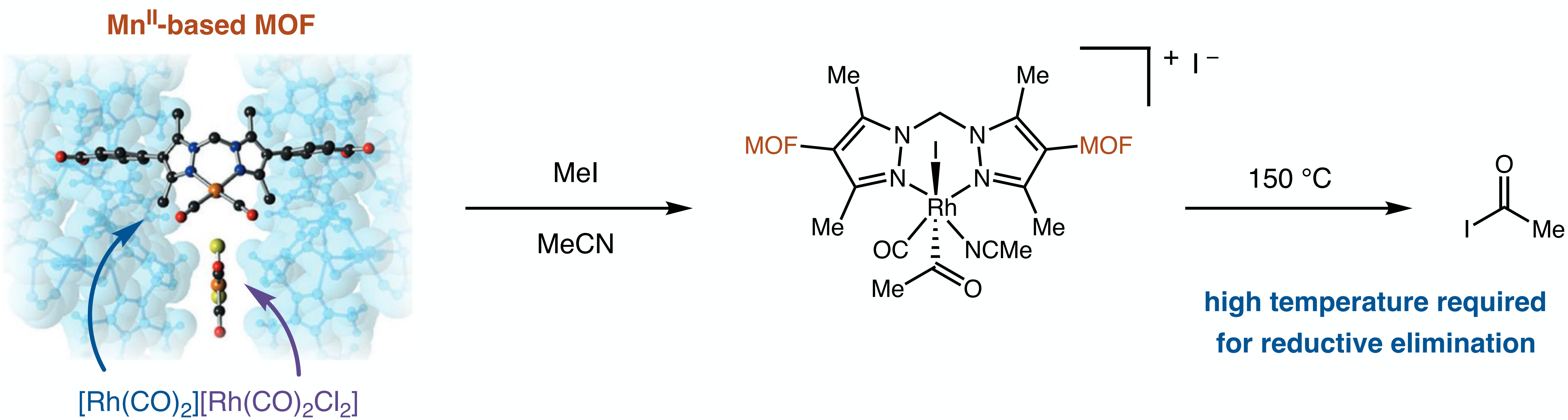


Single-Crystal X-Ray Difrraction (SCXRD) was used to elucidate the mechanism when the catalyst is supported in a MOF

Burgun, A. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 8412-8416.

A Change in Mechanism Upon Site Isolation

Catalytic cycle does not turnover in MOF with methyl iodide



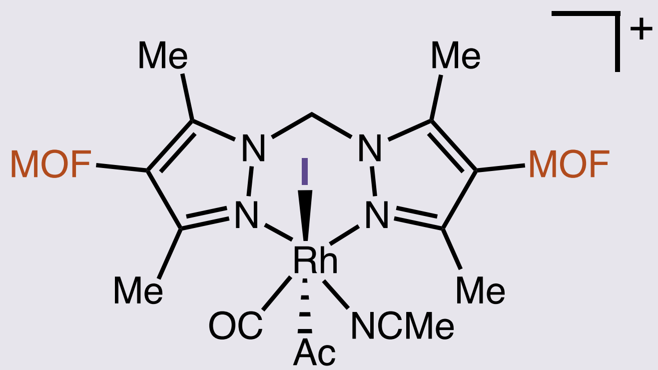
Why?

1. Reductive elimination requires ***cis*** substituents
2. Oxidative addition (S_N2 mechanism) results in ***trans*** substituents
3. Large halide presents a **kinetic barrier to isomerization** in congested MOF pore

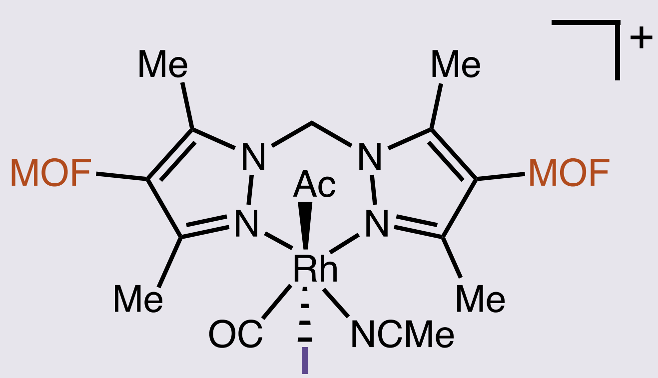
Burgun, A. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 8412-8416.

Evidence for High Barrier to Cis-Trans Isomerization with MeI

Crystal structures show no isomerization to thermodynamic product

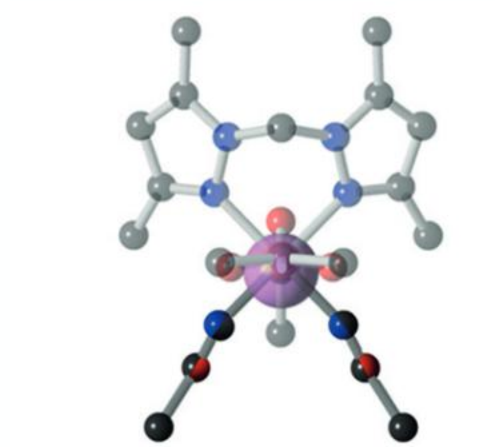


+ (50/50 mixture)

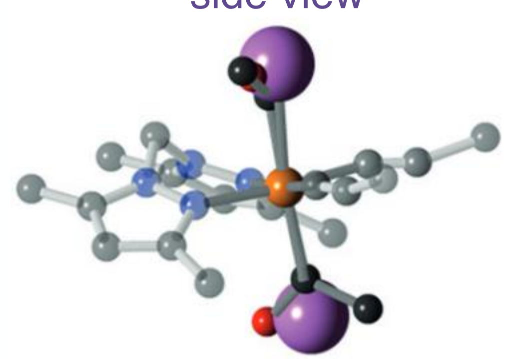


≡

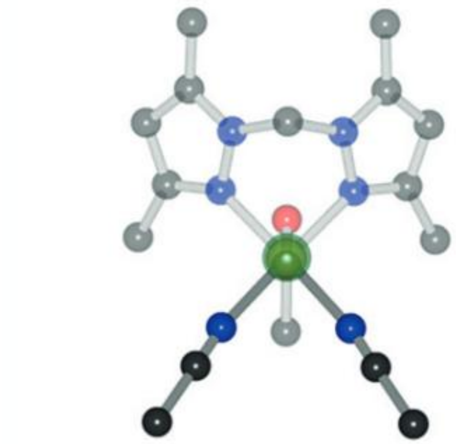
X-Ray



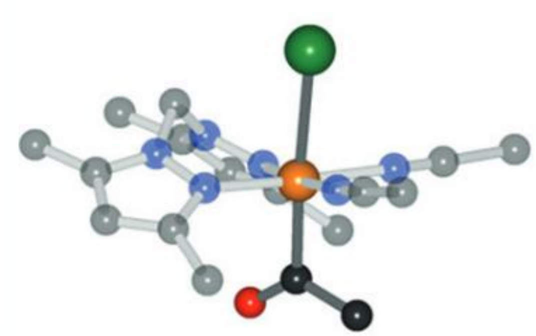
side view



X-Ray



side view



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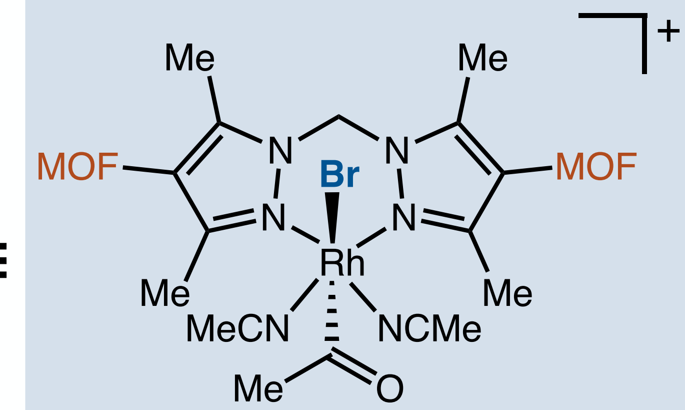


Single oxidative addition product, indicating isomerization

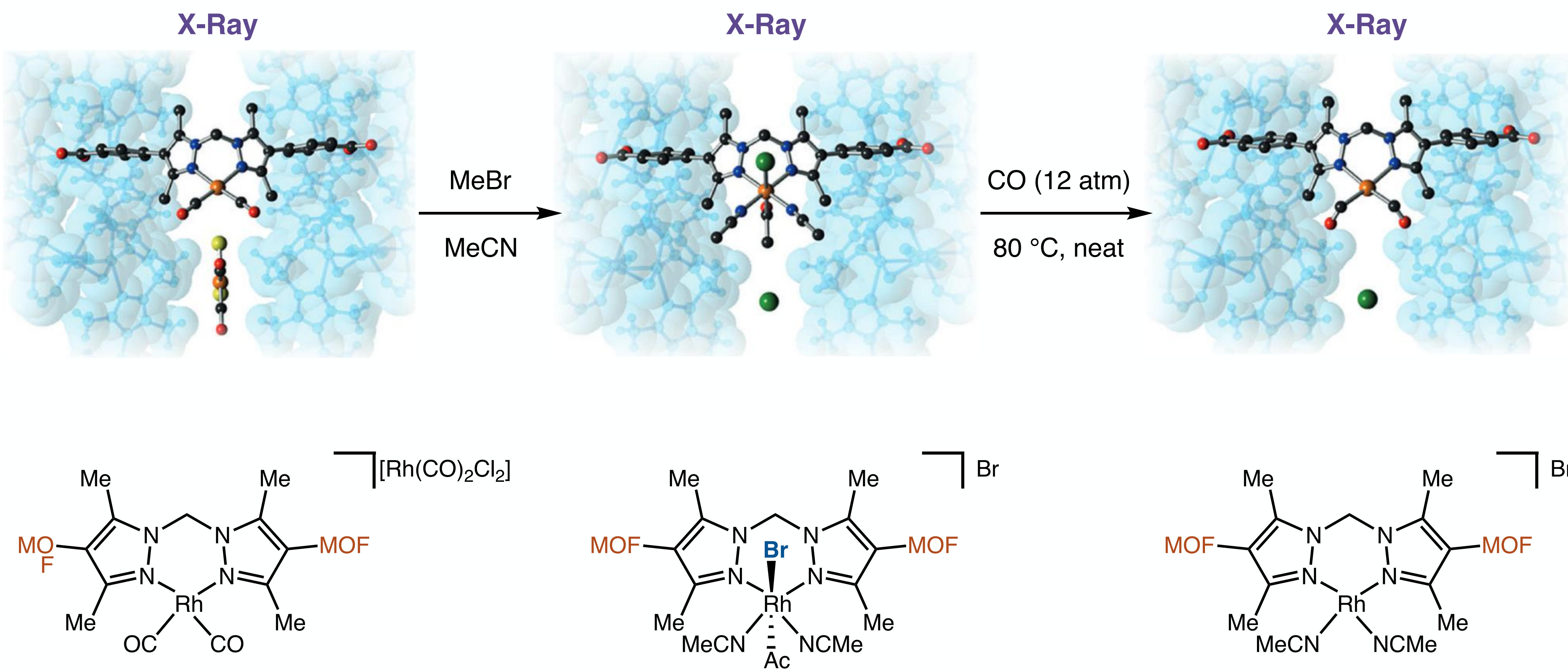
Other isomer unstable in MOF pocket by 4.5 kcal/mol

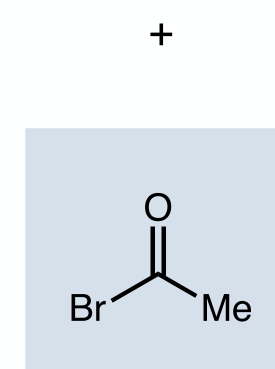
Kinetic product of S_N2 oxidative addition observed (1:1 mixture of *trans* isomers)

Observation of unfavored oxidative addition product suggests a high barrier to isomerization

Burgun, A. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 8412-8416.

Methyl Bromide as an Alternative Substrate



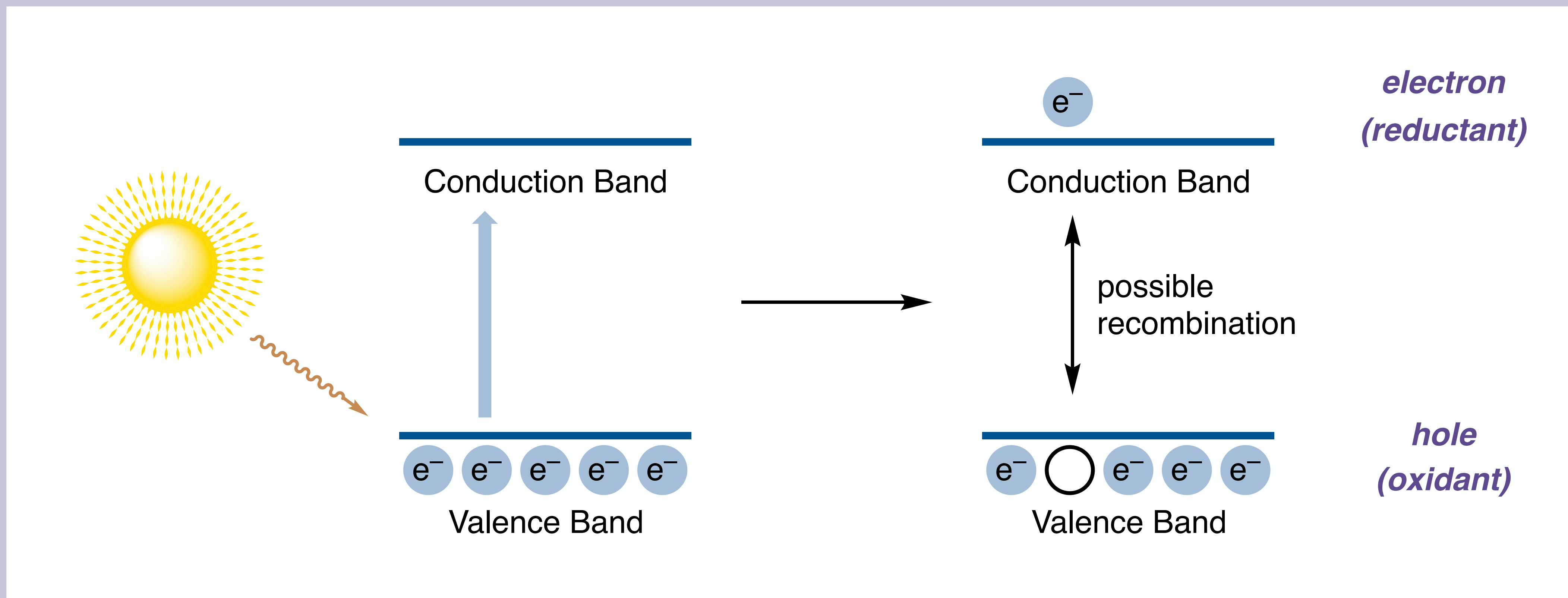


11 turnovers in 10 hours

slow rate attributed to slower oxidative addition for MeBr and isomerization rates in MOF

Burgun, A. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 8412-8416.

Metal-Organic Frameworks as Photocatalysts



A good light harvesting photocatalyst can:

1. Absorb the abundant light in the solar spectrum (visible and near IR)
2. Maintain a charge-separated state long enough to perform productive chemistry

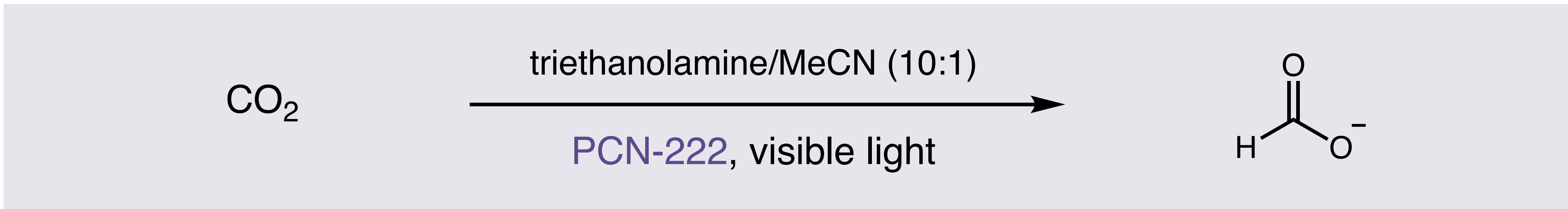
MOF structures are well-defined and infinitely tunable,

making them ideal for systematic photocatalyst development

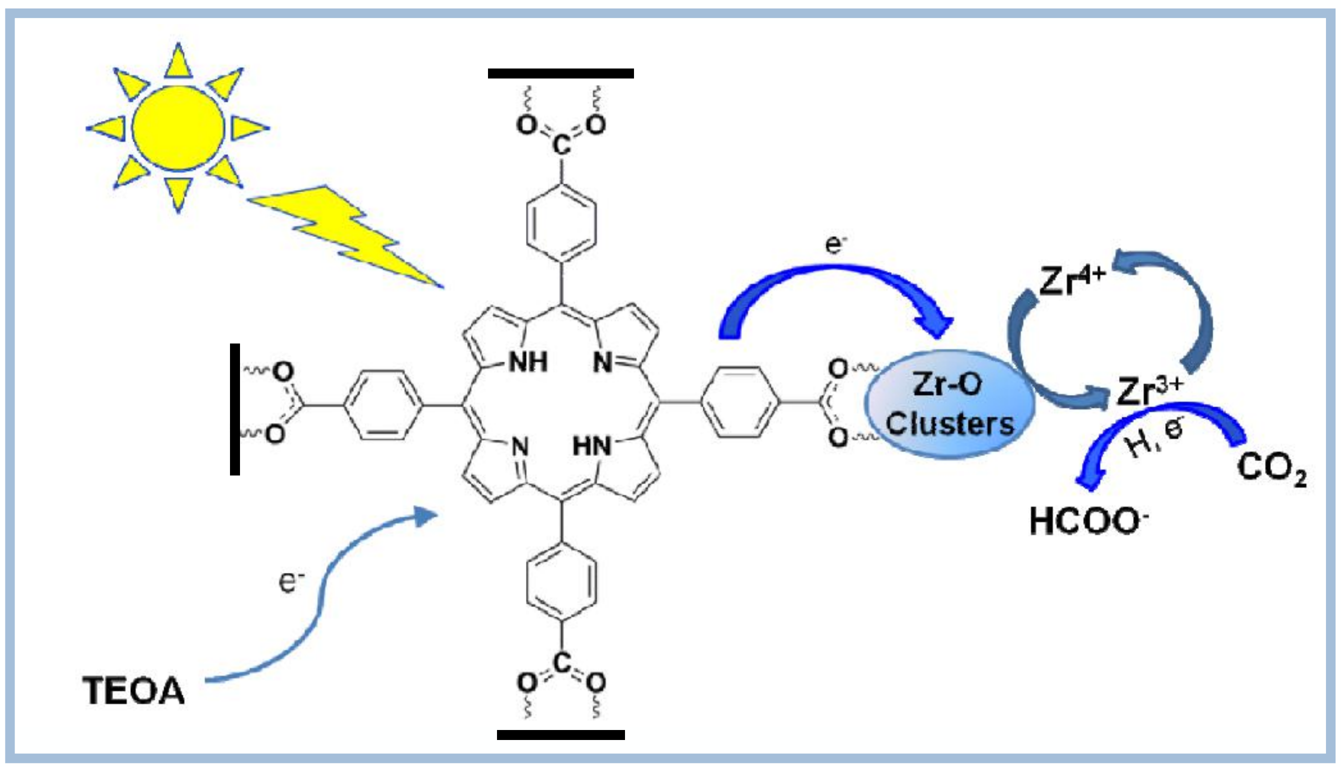
Xiao, J.-D.; Jiang, H.-L. *Acc. Chem. Res.* **2019**, *52*, 356-366.

Tuning of Organic Linker to Absorb Visible Light

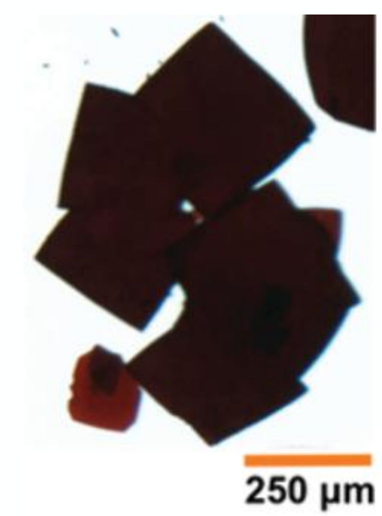
Desirable chemical transformation



Converts greenhouse gas to useful chemical feedstock



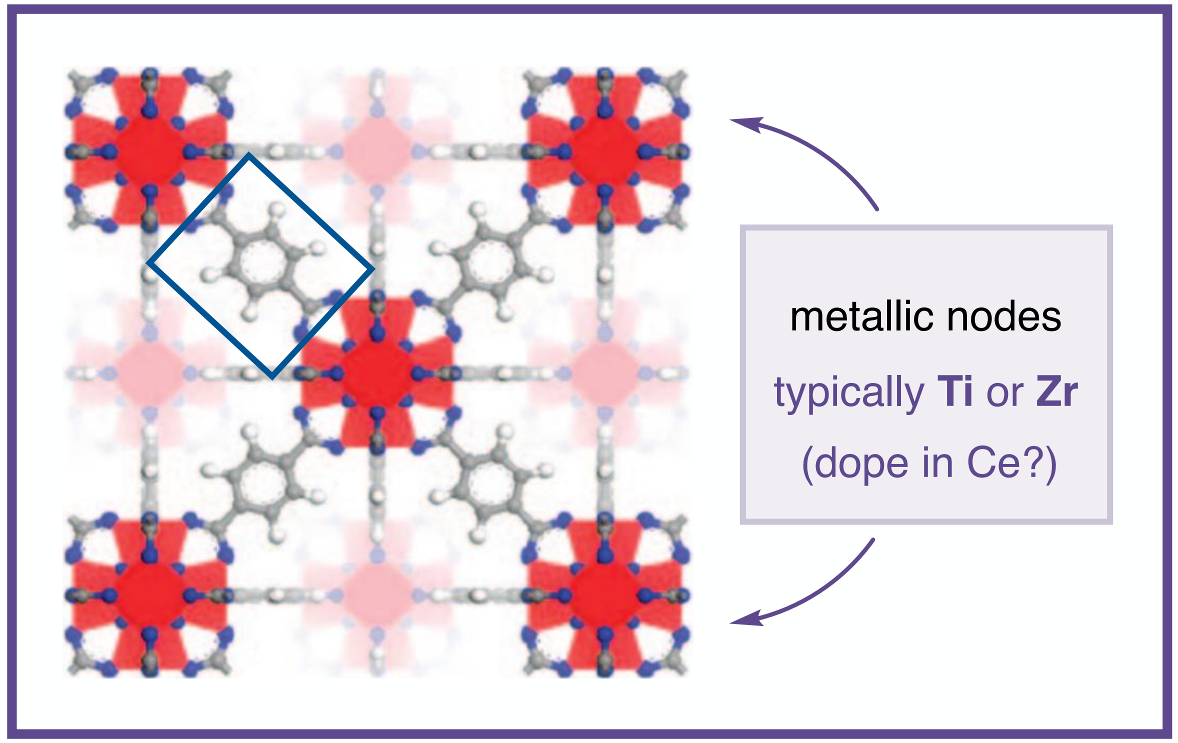
Porphyrin linkers enable harvest of abundant visible light to perform chemistry



Lee, C. Y.; Farha, O. M.; Hong, B. J. Sarjeant, A. A.; Nguyen, S. B. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858-15861.

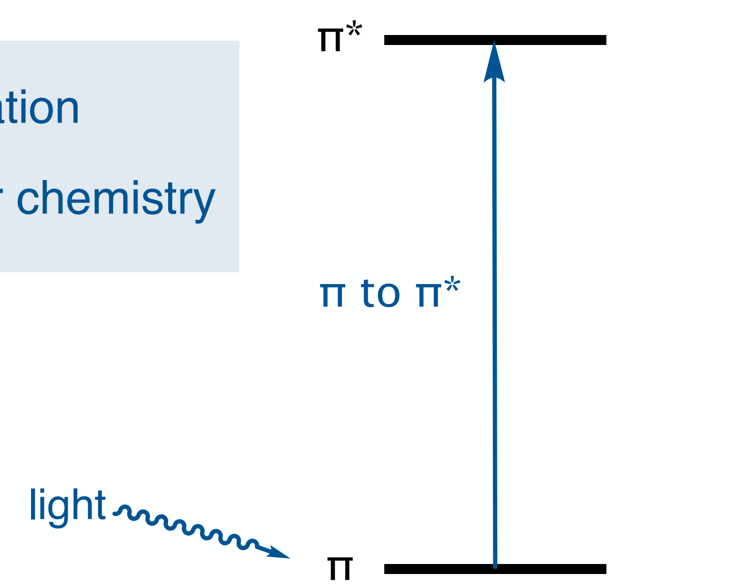
Xu, H.-Q.; Hu J.; Wang, D.; Li, Z.; Zhang, Q.; Luo, Y.; Yu, S.-H.; Jiang, H.-L. *J. Am. Chem. Soc.* **2015**, *137*, 13440-13443.

Lanthanide Doping to Promote Electron-Hole Separation



Minimal electron-hole separation

recombination occurs before other chemistry



linker-centered orbitals

Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. *J. Am. Chem. Soc.* **2018**, *140*, 7904-7912.

Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. *J. Chem. Phys.* **2019**, *150*, 041701.

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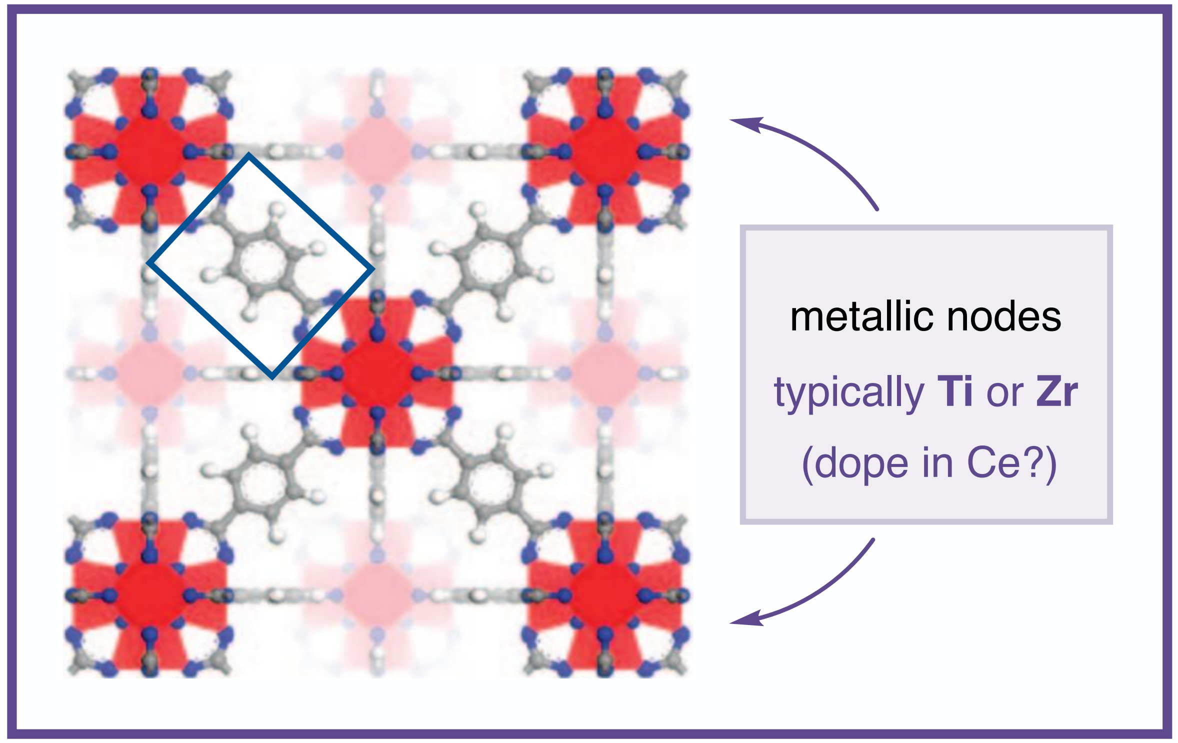

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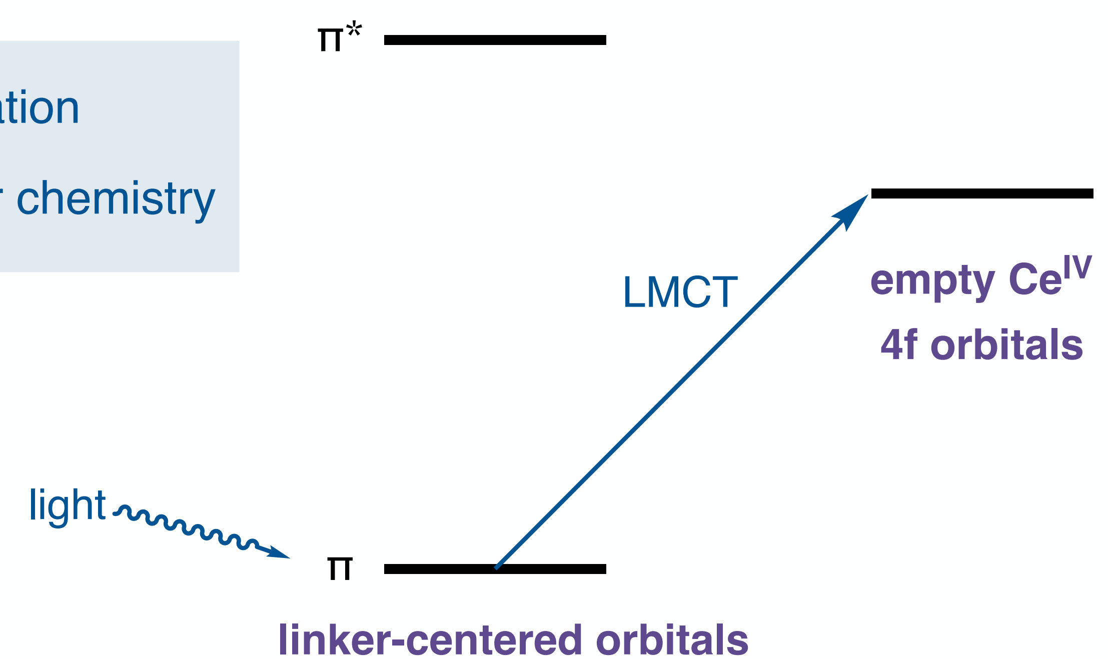


Charges are separated and recombination is delayed

Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. *J. Am. Chem. Soc.* **2018**, *140*, 7904-7912.
Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. *J. Chem. Phys.* **2019**, *150*, 041701.

Upconversion to Access Whole-Spectrum Hydrogen Evolution

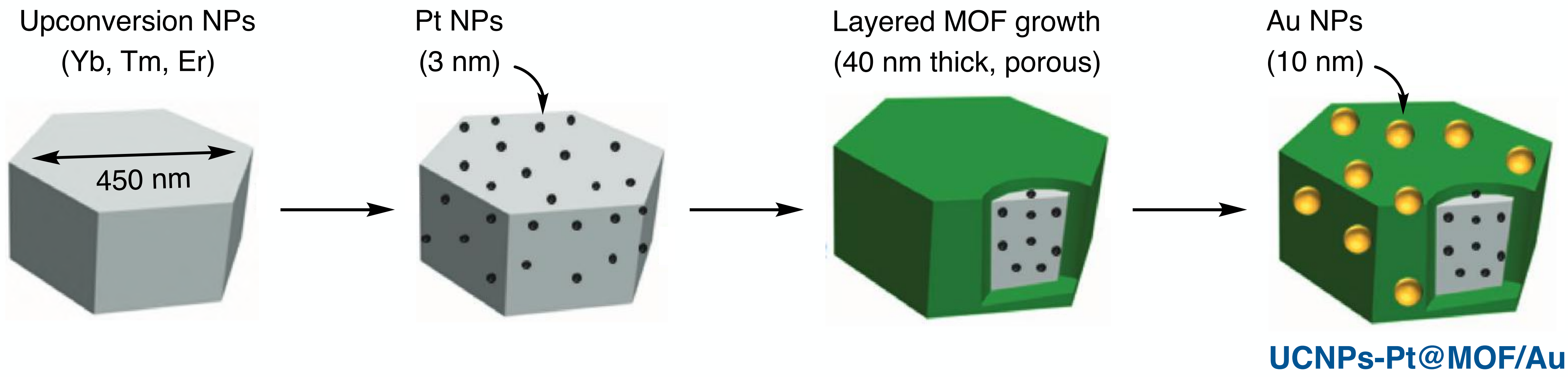
Ideal Hydrogen Evolution Reaction (HER):

$$H_2O \xrightarrow{\text{visible/near IR light}} H_2$$

Near IR and visible light compose ~95% of the solar spectrum

Few photocatalysts can utilize low energy light

Composite Material Synthesis



Multiple mechanistic pathways allow use of entire solar spectrum for hydrogen evolution reaction

Li, D.;Yu, S.-H.; Jiang, H.-L. *Adv. Mater.* **2018**, *30*, 1707377.

Upconversion to Access Whole-Spectrum Hydrogen Evolution

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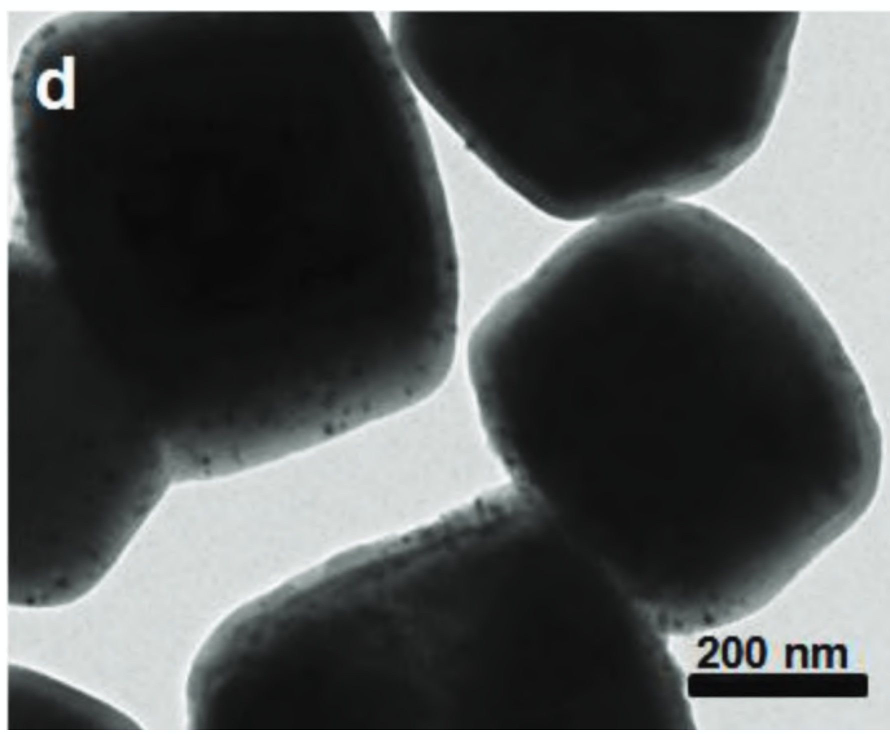
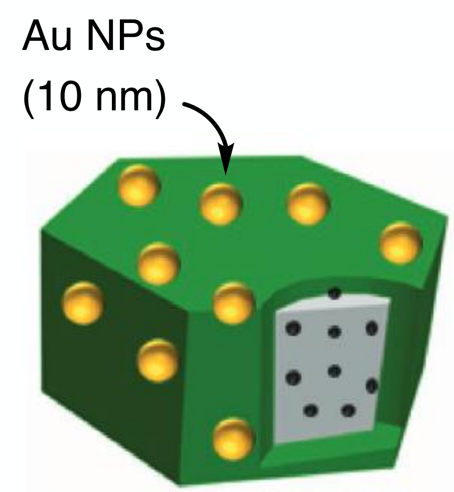


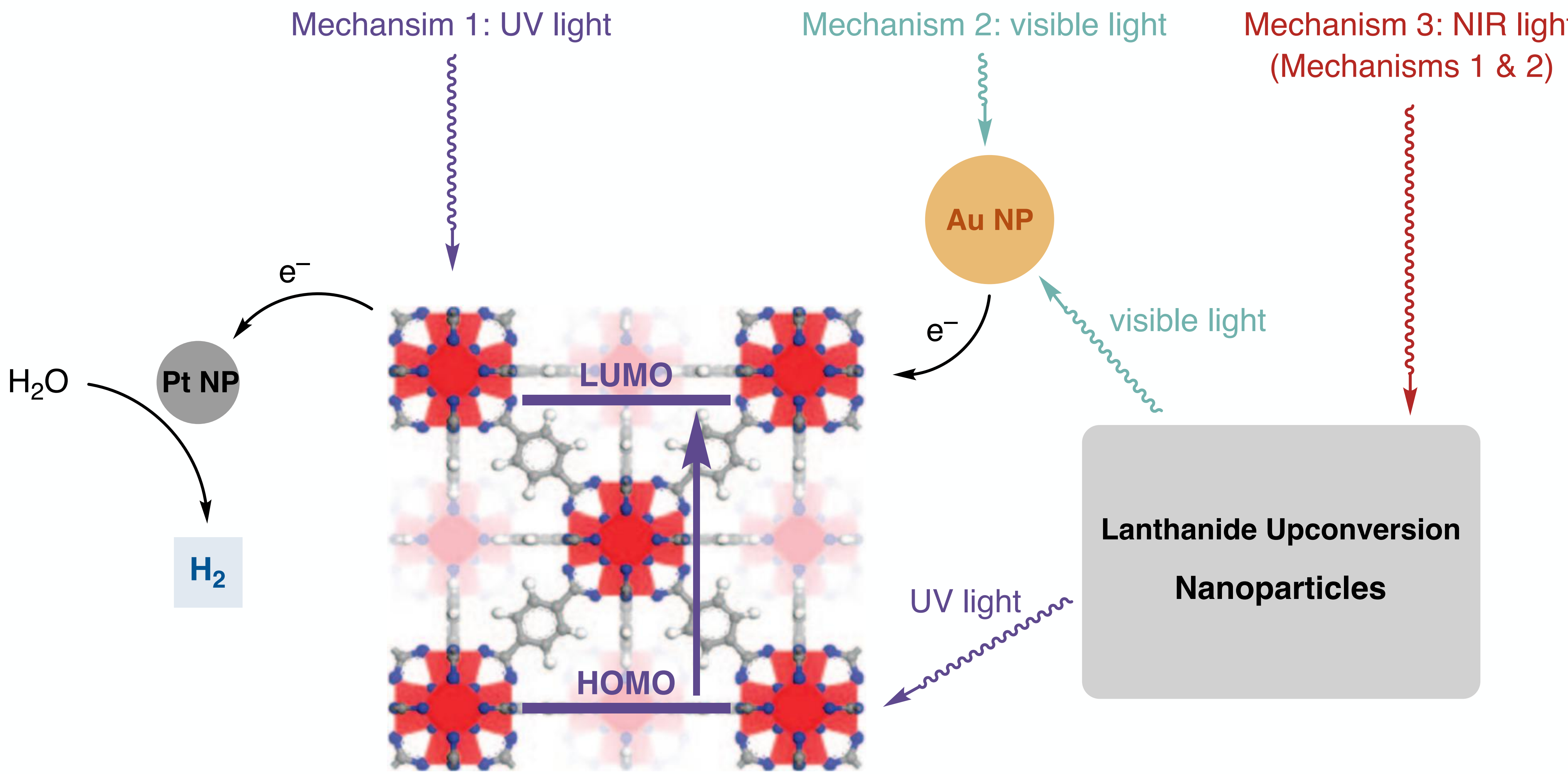


UCNPs-Pt@MOF/Au

Multiple mechanistic pathways allow use of entire solar spectrum for hydrogen evolution reaction

Li, D.;Yu, S.-H.; Jiang, H.-L. *Adv. Mater.* **2018**, *30*, 1707377.

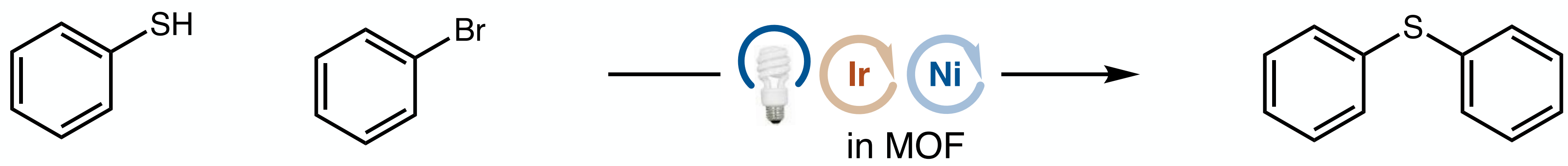
Upconversion to Access Whole-Spectrum Hydrogen Evolution



Mechanistic redundancy allows for highly efficient H_2 evolution (280 μmol $g^{-1}h^{-1}$) under solar spectrum

Li, D.;Yu, S.-H.; Jiang, H.-L. *Adv. Mater.* **2018**, *30*, 1707377.

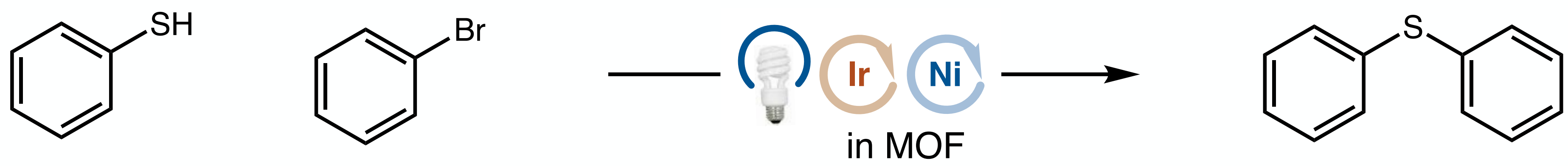
Metallaphotoredox in MOFs (MetallaPhotoMOFs)

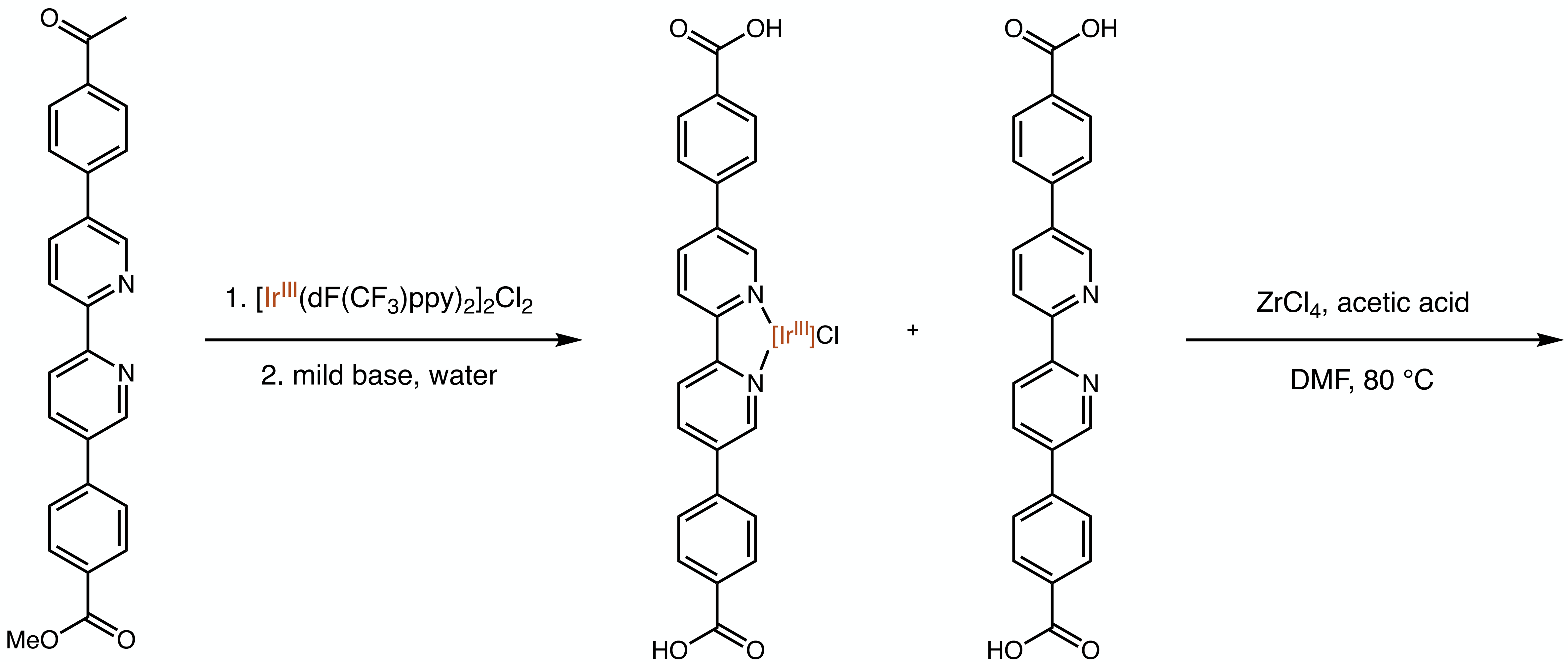


For a more complete review of post-synthetic modifications of MOFs: Cohen, S. M. *J. Am. Chem. Soc.* **2017**, *139*, 2855-2863.

Zu, Y.-Y.; Lan, G.; Fan, Y.; Veroneau, S. S.; Song, Y.; Micheroni, D.; Lin, W. *Angew. Chem. Int. Ed.* **2018**, *130*, 14286–14290.

Dual-Functionalized MOF Synthesis





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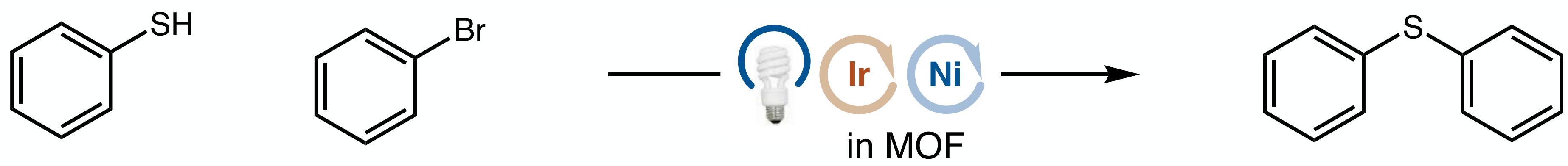

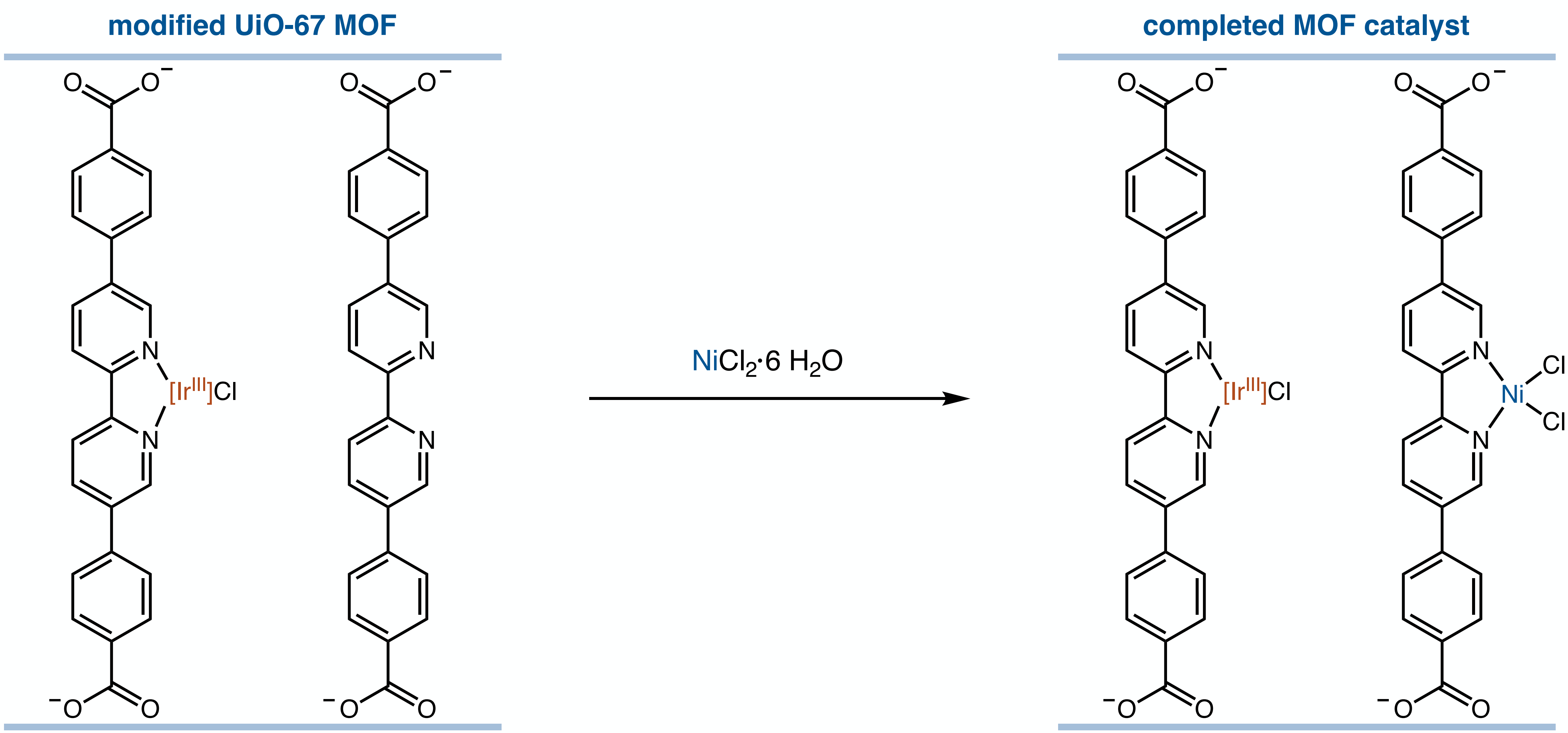

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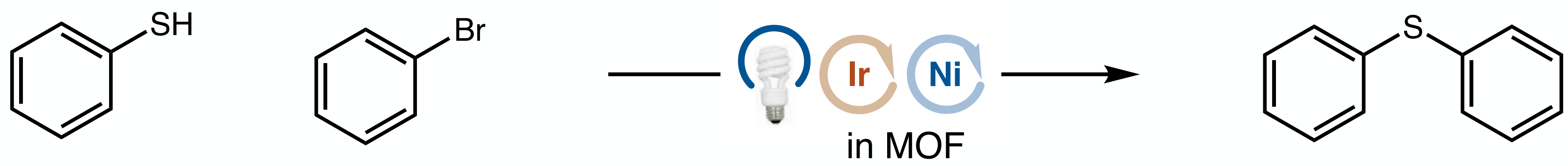
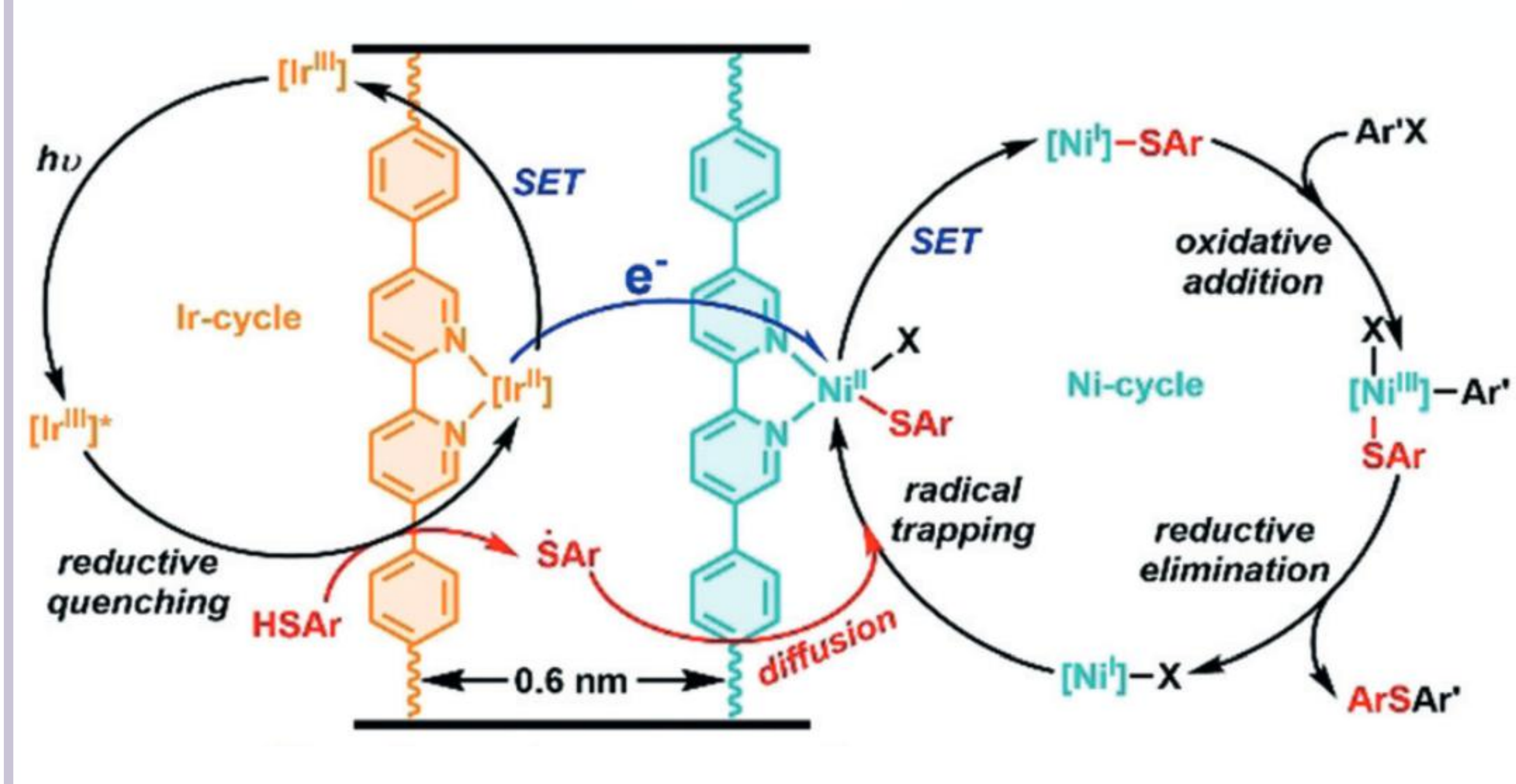


Lower loadings (0.002 mol%), higher TON (38,500) than homogeneous system

Proximity facilitates electron transfer between catalysts

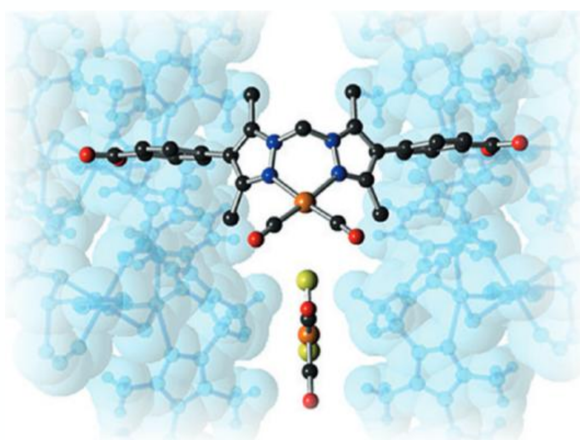
Only application of MOFs to metallaphotoredox catalysis

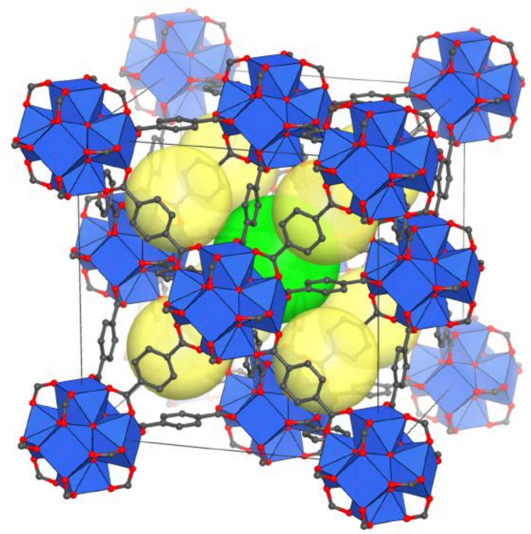
Mechanism

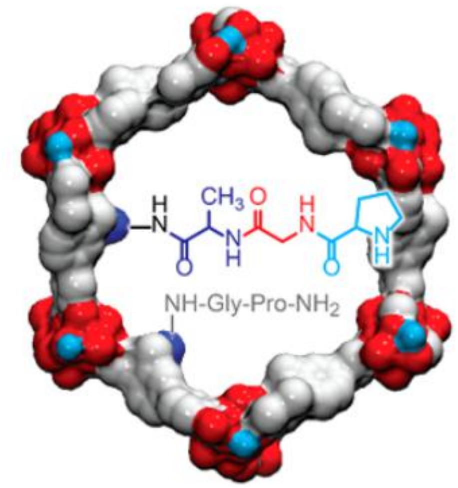


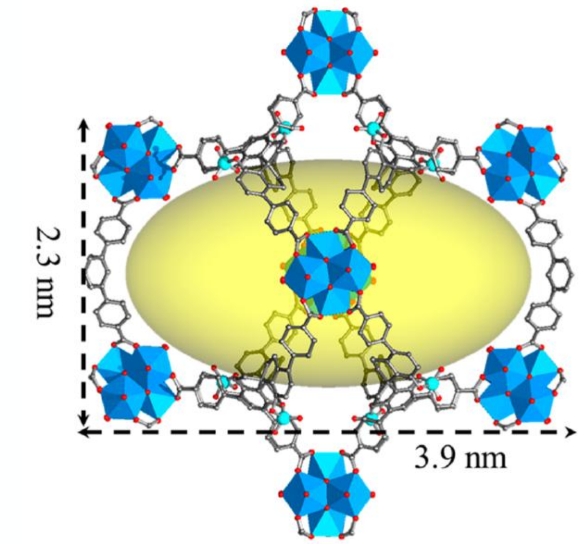
Zu, Y.-Y.; Lan, G.; Fan, Y.; Veroneau, S. S.; Song, Y.; Micheroni, D.; Lin, W. *Angew. Chem. Int. Ed.* **2018**, *130*, 14286–14290.

Outlook









MOFs rationally designed for catalysis, not structural aesthetics

Identification of robust MOF classes amenable to structural modification

Participation of a greater number of organic-focused research groups