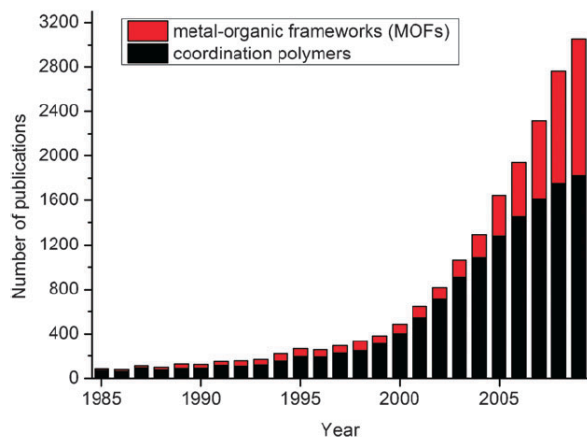


Metal Organic Frameworks and Covalent Organic Frameworks

Permanently Porous, Crystalline Materials

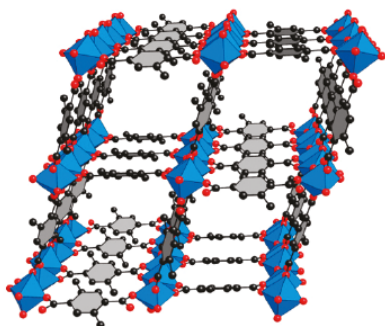


permanent microporosity:

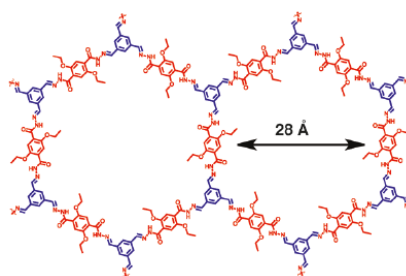
retaining < 2nm dimensional channels
after vacuum evacuation of the solvent

crystallinity:

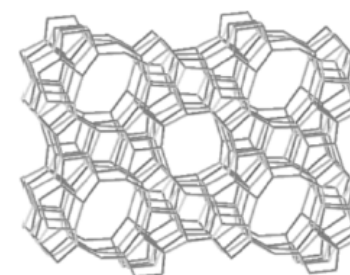
provides a regular, rigid structure
readily analyzed by x-ray diffraction



Metal Organic Frameworks



Covalent Organic Framework

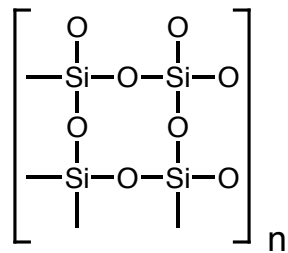


Zeolite

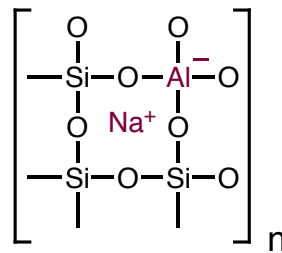
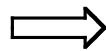
Tailoring of the organic component provides the ability to molecularly design porous materials.

Zeolites: Crystalline Microporous Materials

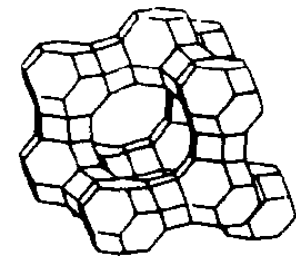
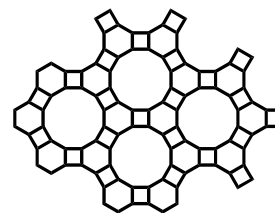
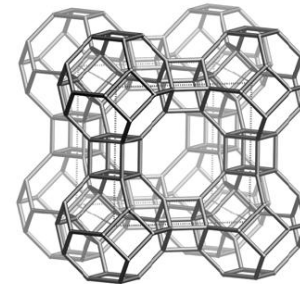
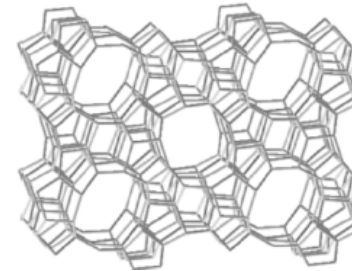
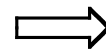
- Mixed anionic polymer Si and Al oxides



Silica



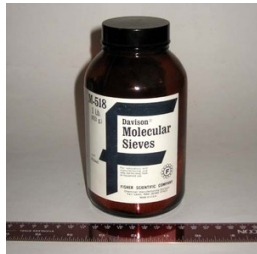
Aluminosilicate



Variation of counterion and Si/Al ratio provides the basis for broad array of microporous structures

Zeolites: Crystalline Microporous Materials

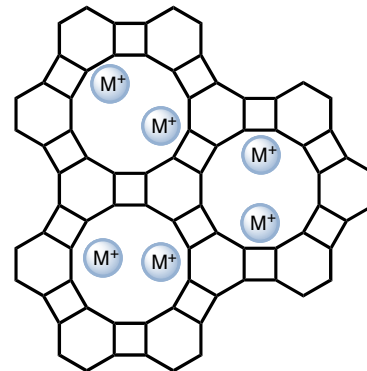
- Permanent microporosity—pore structure survives vacuum evacuation



adsorption

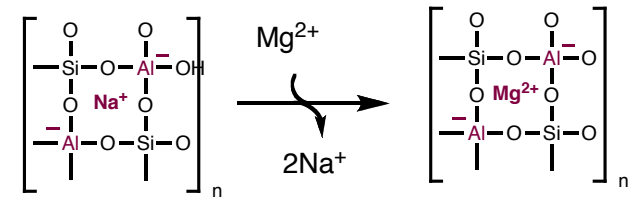


catalysis

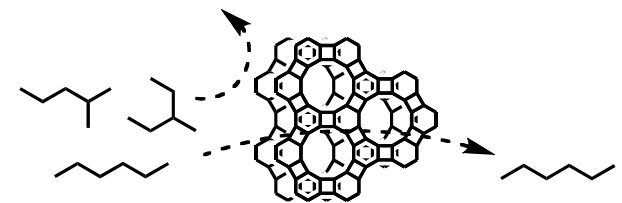


< 2 nm

regular porous network,
consistent pore size
and shape



ion exchange

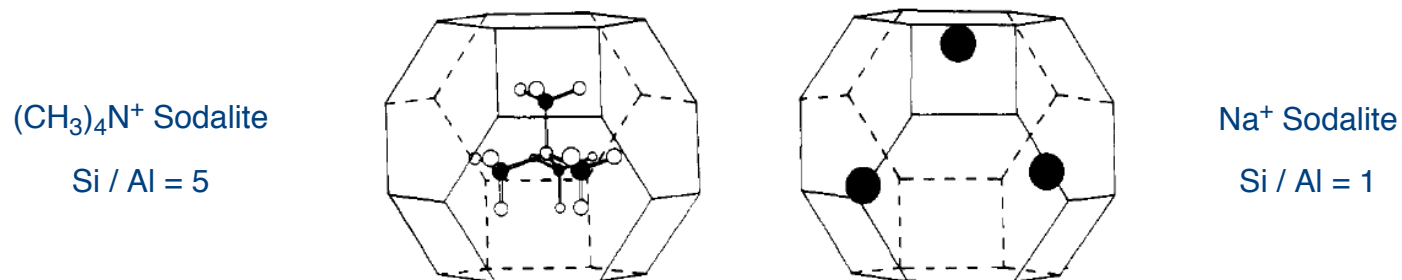


separations

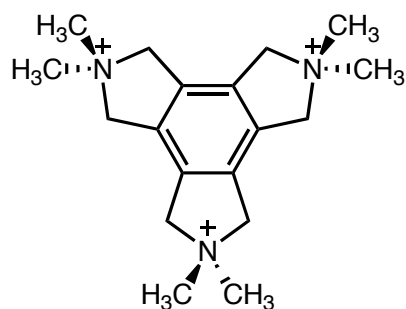
>10 million tons consumed annually for industrial uses

Designing Novel Zeolites

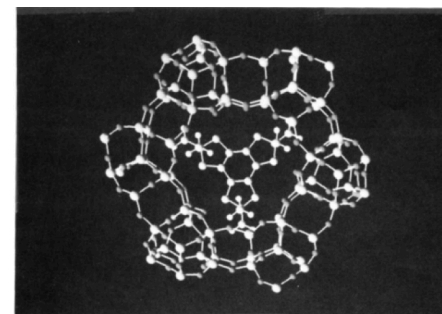
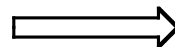
- Adjustment of the Si : Al ratio controls the framework charge, but also alters the structure



- Counterion can direct pore shape/symmetry but unpredictable control over long-range structure



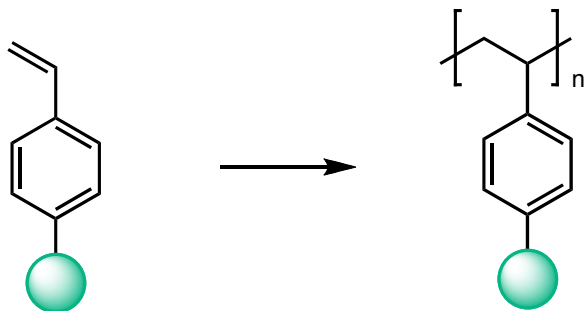
**structurally
complex cation**



**templated
pore structure**

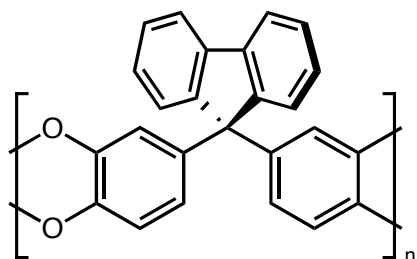
The complex relationship between framework structure and composition limits chemical design.

Organic Polymers

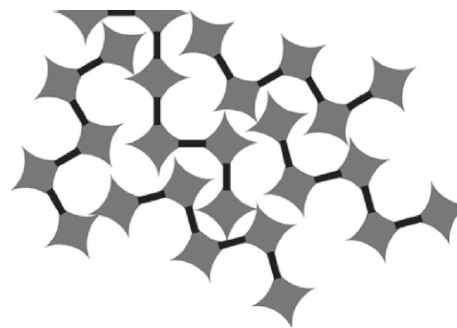


- Predictable design of molecular functionality into materials
- Limited control over long range structure

- Polymer design can produce intrinsic microporosity, but not regular pore structure



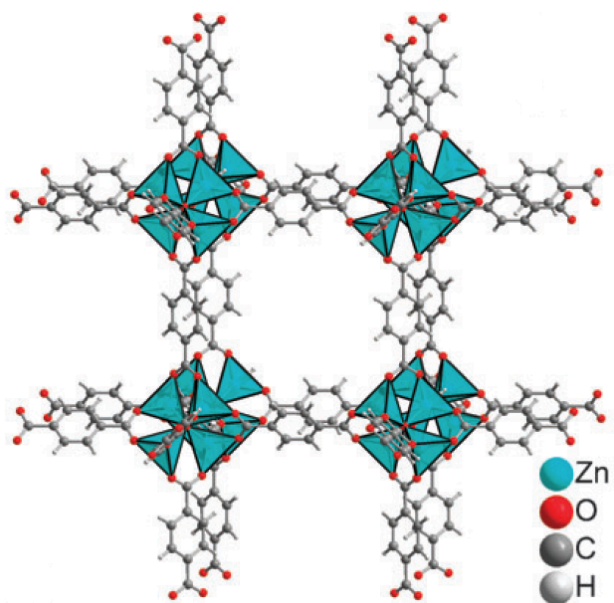
**polymer of intrinsic
microporosity**



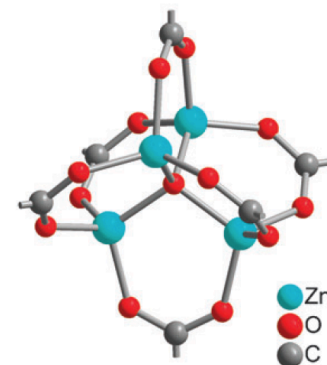
**partially ordered
pore structure**

Metal Organic Frameworks

Combining Molecular Design and Structural Order

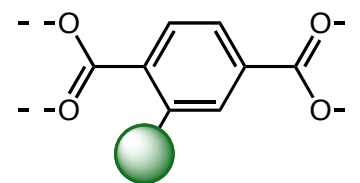


Metal Organic Framework



Inorganic Node

- Geometrical versatility
- Structural regularity

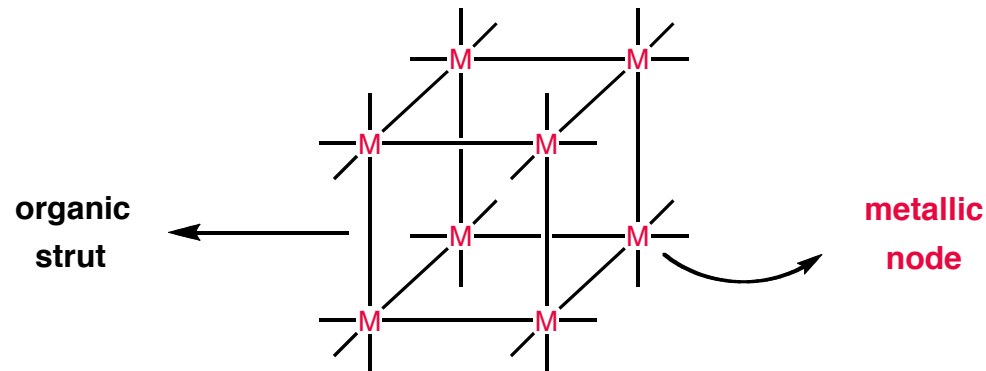


Organic Strut

- Synthetic versatility
- Modular functionality

Metal Organic Frameworks

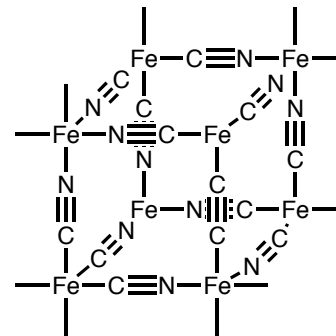
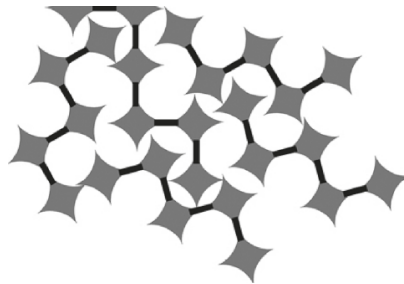
Nodes and Struts



a simplified representation of MOFs

- Strong, irreversible bond formation only produces ordered structures in simple cases

irreversible bond
=
kinetic control
■ defect propagation
■ poor crystallinity

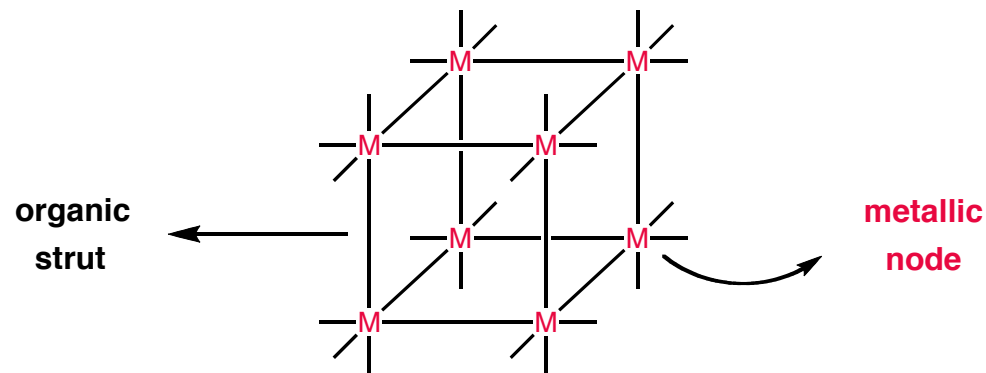


$\text{Fe}_7(\text{CN})_{18}$
Prussian Blue
■ simple node / strut
MOF based on strong,
directional coordination

Labile linking is required for thermodynamic control in lattice structures.

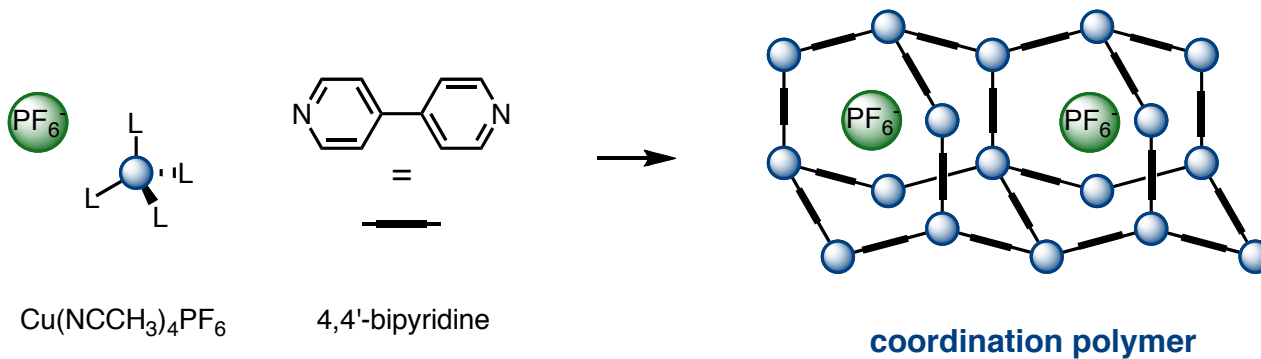
Metal Organic Frameworks

Nodes and Struts



a simplified representation of MOFs

- Weak, labile bonds form regular structures but lack structural and chemical integrity

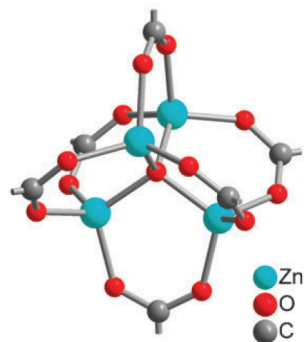


- Water, acid instability
- Many structures do not survive desolvation = lack permanent microporosity

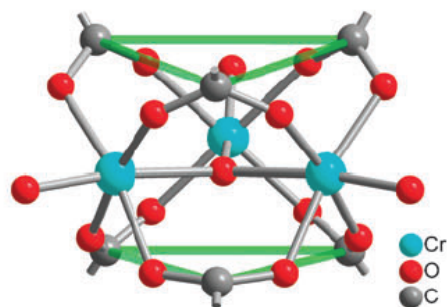
Resilient structures require stronger linkages.

The Secondary Building Unit

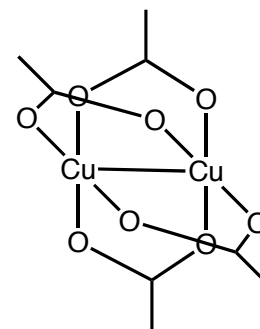
Strong Nodes Composed of Multiple Labile Bonds



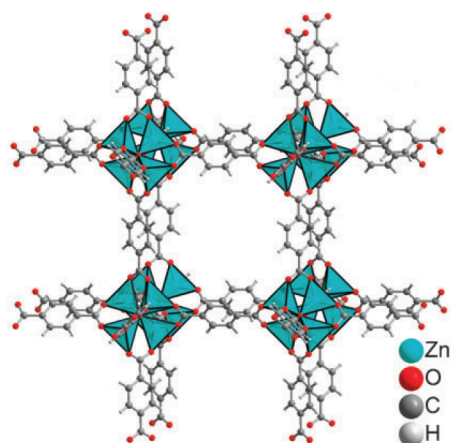
$\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6$
octahedral node



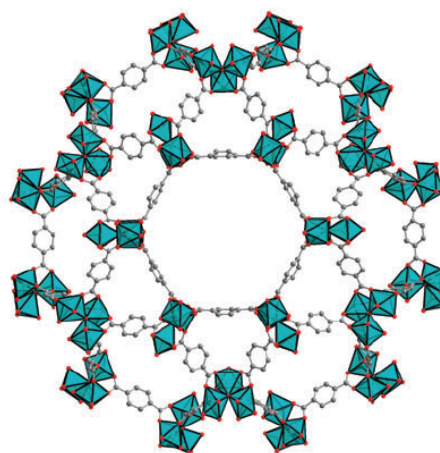
$\text{Cr}_3(\text{O})(\text{F})(\text{OH}_2)_2(\text{O}_2\text{CR})_6$
prismatic node



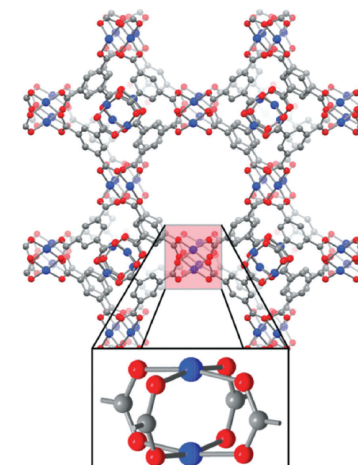
$\text{Cu}_2(\text{O}_2\text{CR})_4$
square planar node



$\text{Zn}_4\text{O}(\text{bdc})_3$
MOF-5



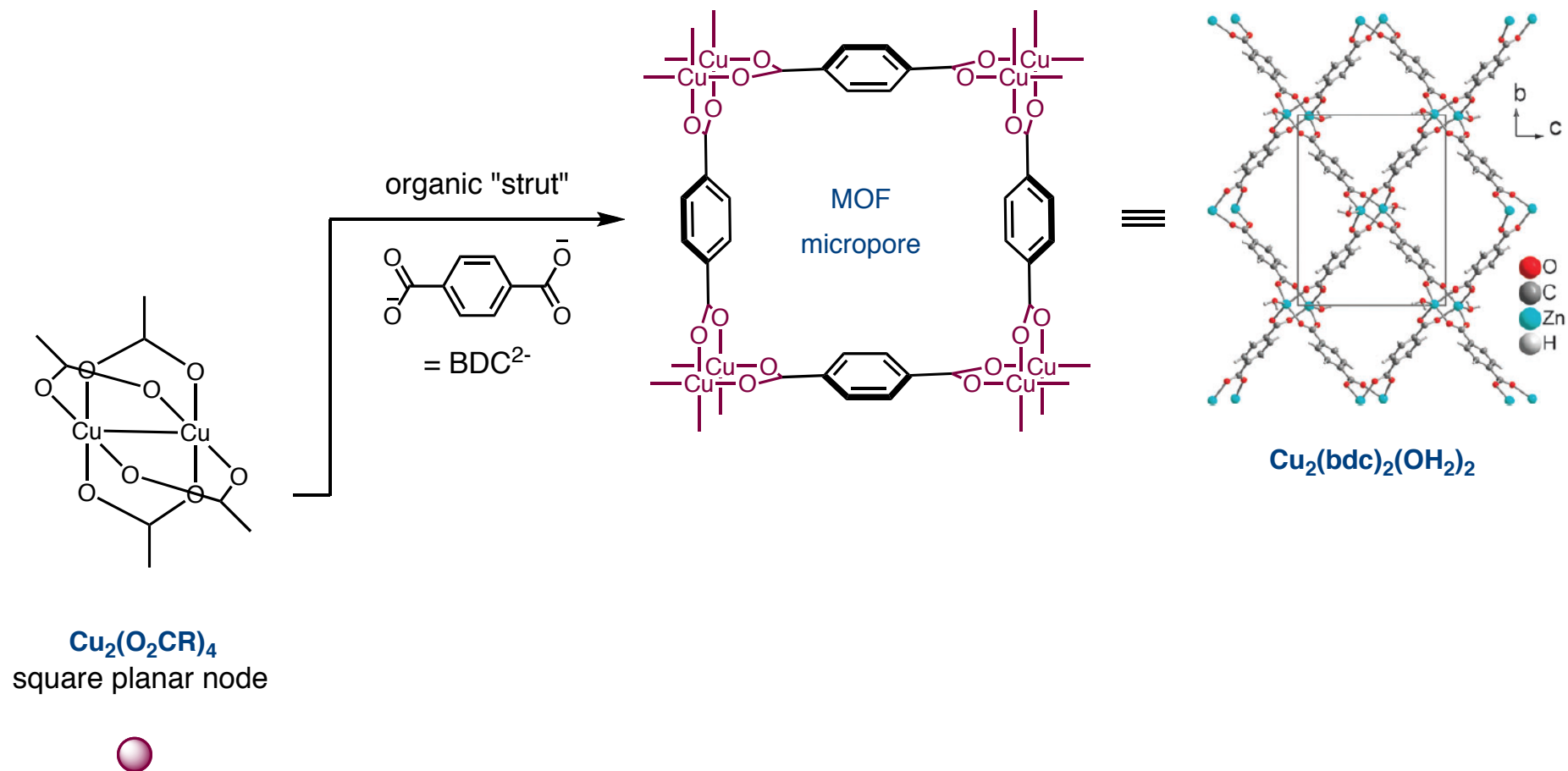
$\text{Cr}_3(\text{O})(\text{bdc})_3(\text{F})(\text{OH}_2)_2$
MIL-101



$\text{Cu}_3(\text{btc})_2$

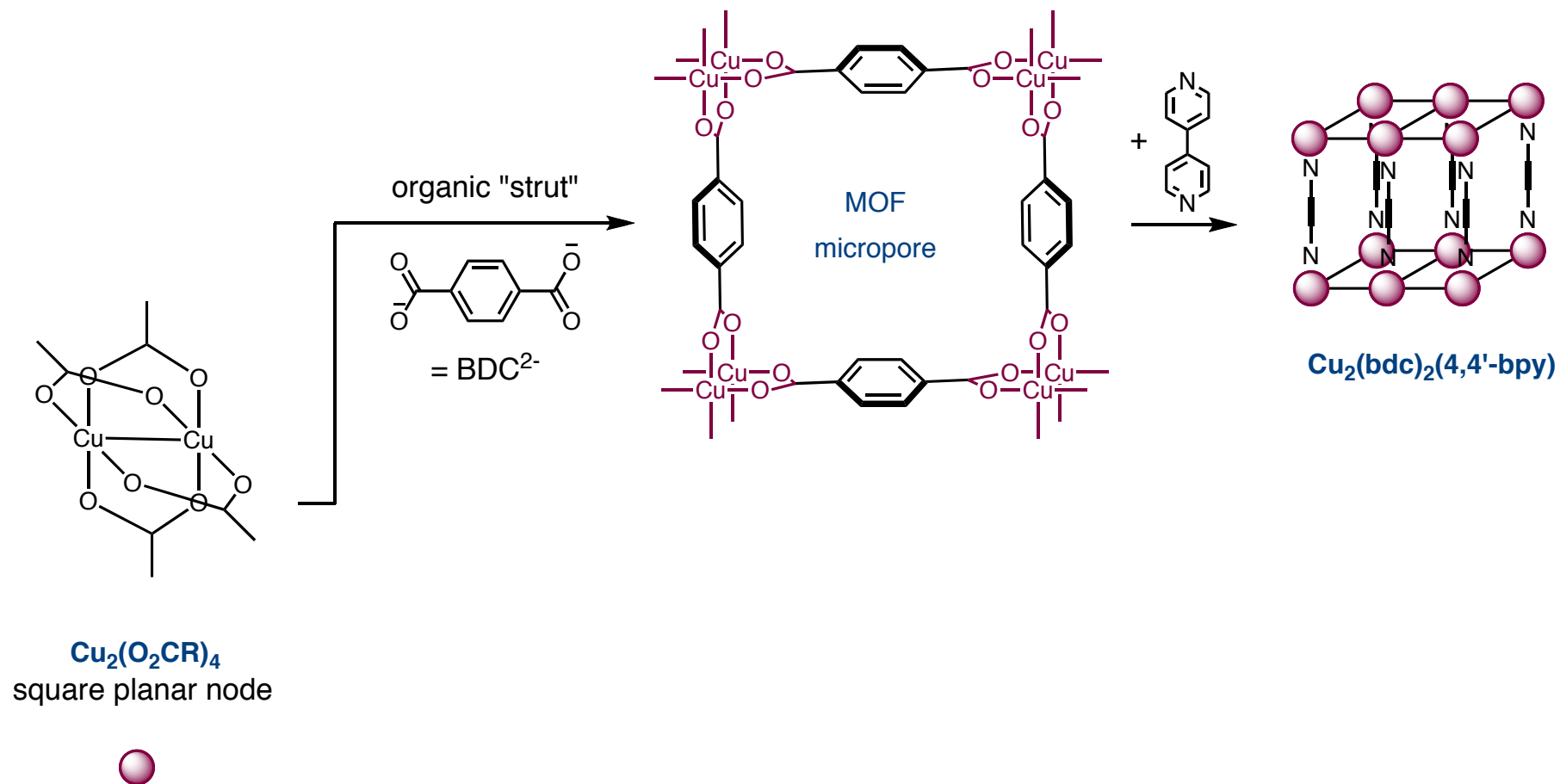
The Secondary Building Unit

Two- versus Three-Dimensional Frameworks



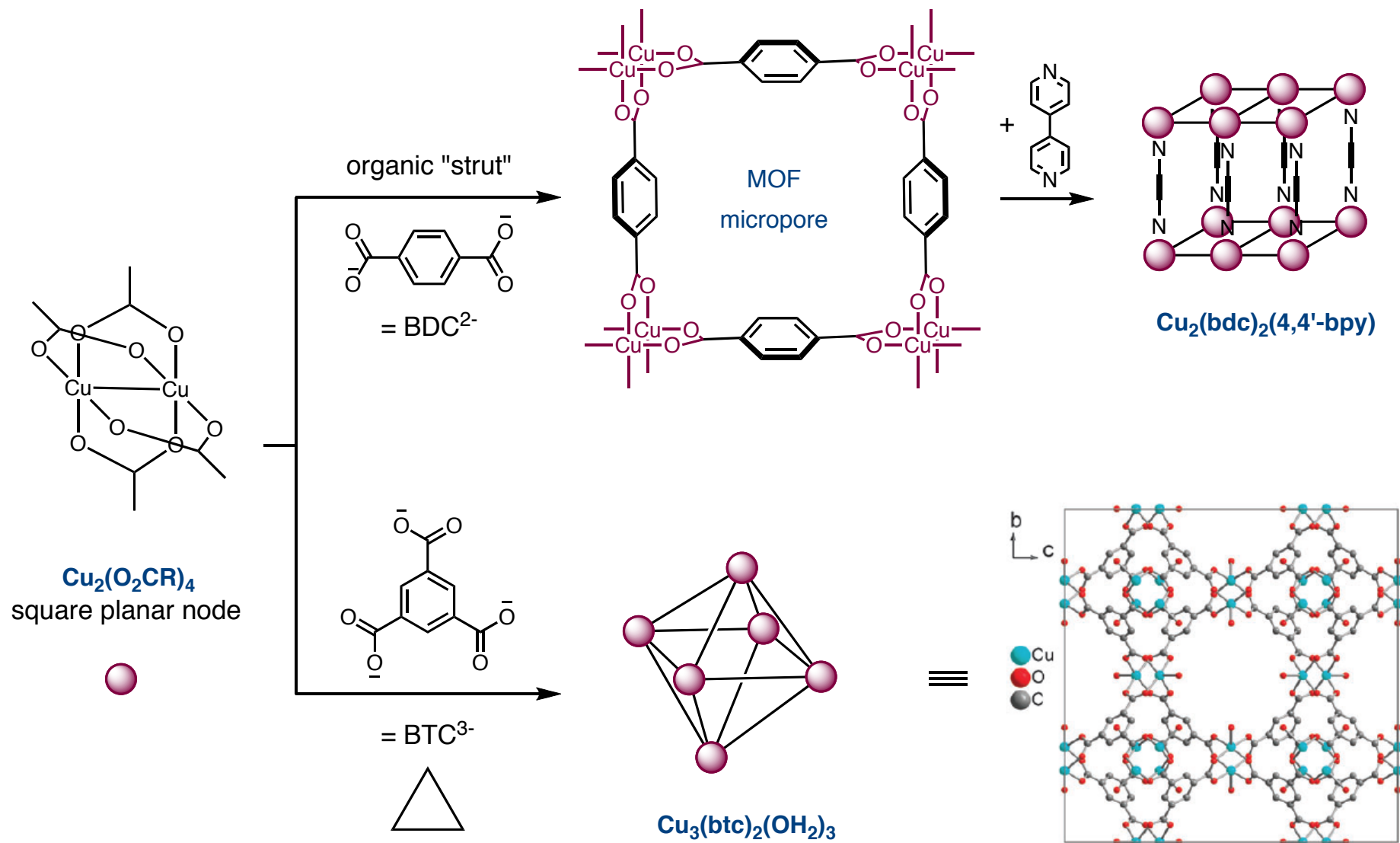
The Secondary Building Unit

Two- versus Three-Dimensional Frameworks



The Secondary Building Unit

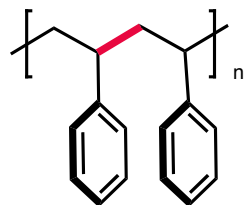
Two- versus Three-Dimensional Frameworks



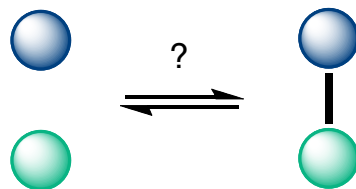
Covalent Organic Frameworks

Regular networks of p-block elements

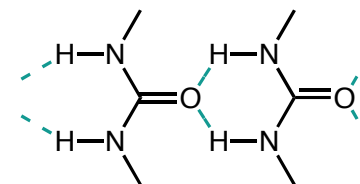
- Bond strength and reversibility—how to balance durability and thermodynamic control



irreversible linkage =
kinetic control

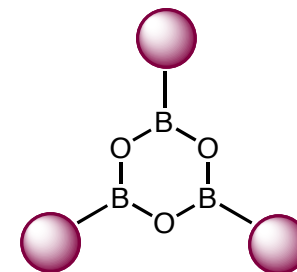
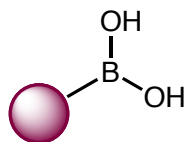


reversible covalent bond



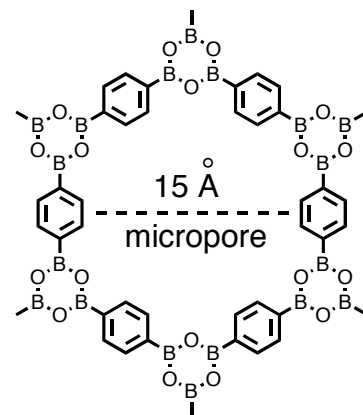
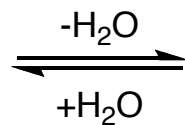
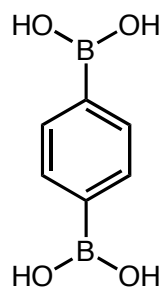
weak bonds =
structural fragility

- Cote and coworkers take advantage of thermal dehydration of boronic acids

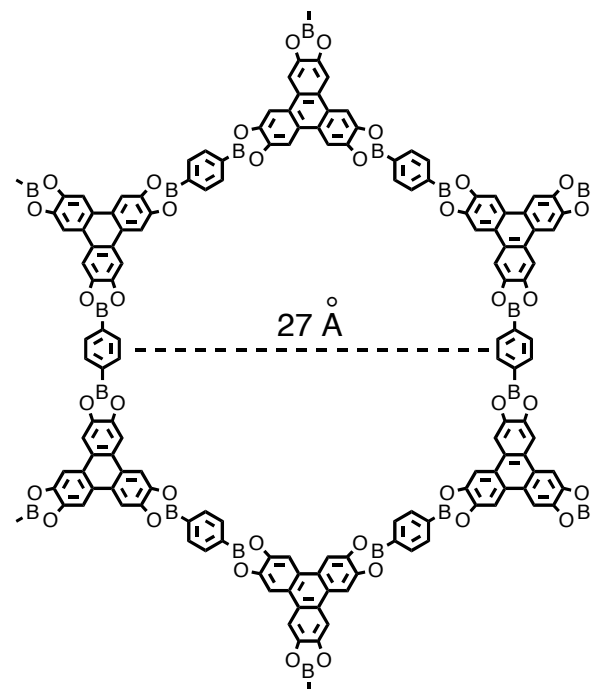
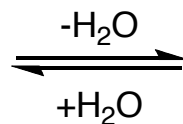
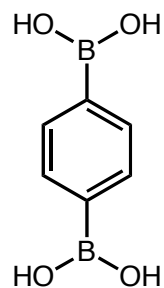
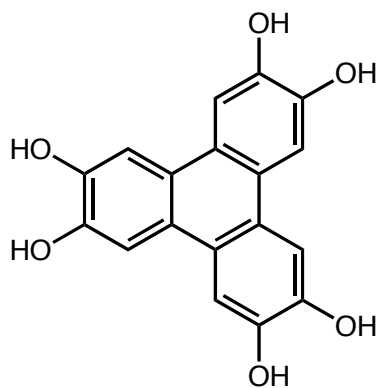


Covalent Organic Frameworks

2D Networks Based on Diboronic Acids



COF-1
boroxine
anhydride

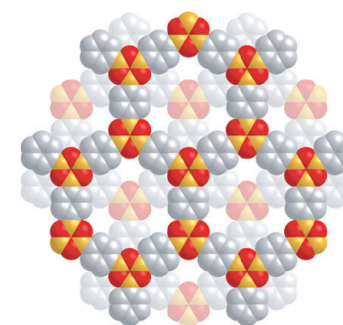
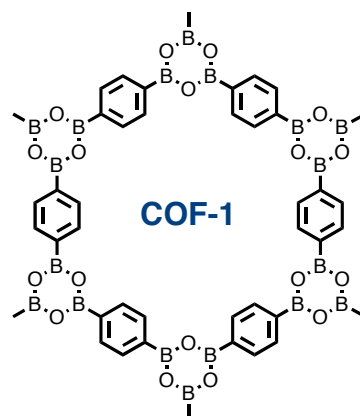


COF-5
boronate
ester

Covalent Organic Frameworks

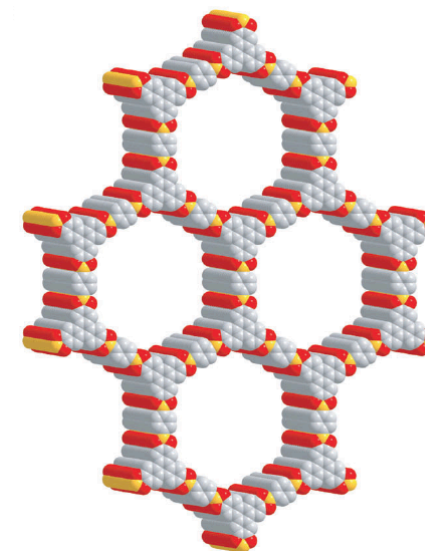
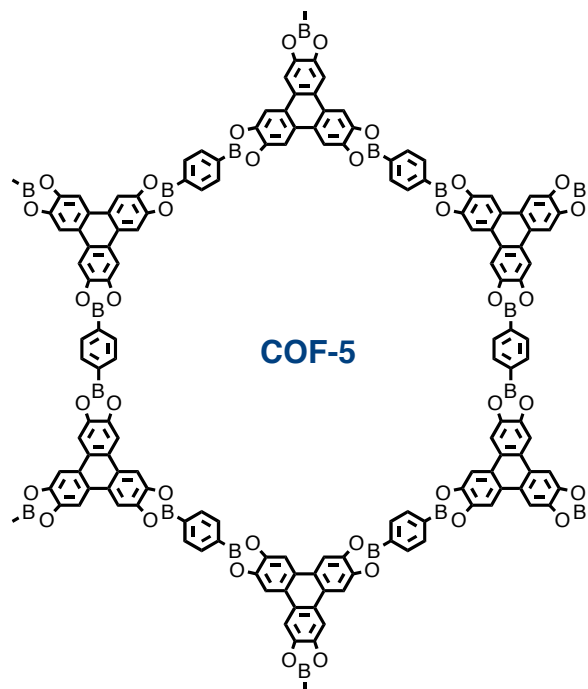
2D Networks Based on Diboronic Acids

- weak interlayer dispersion
- sterics and templation by the solvent are invoked as more subtle effects



"staggered" layering

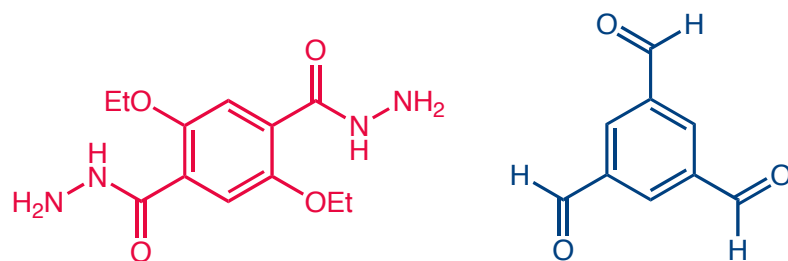
- strong dispersion forces between overlapping triphenylene units
- more common and more useful layering pattern



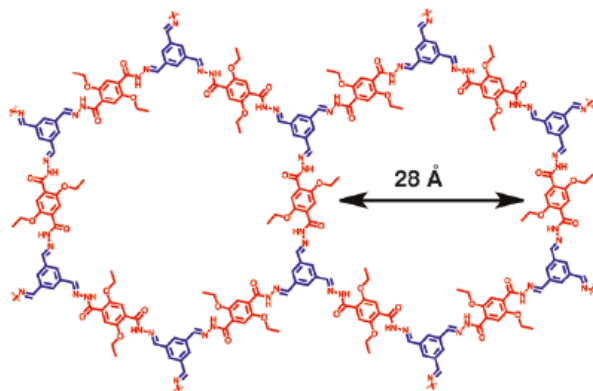
"eclipsed" layering

Hydrazone-Linked Covalent Organic Frameworks

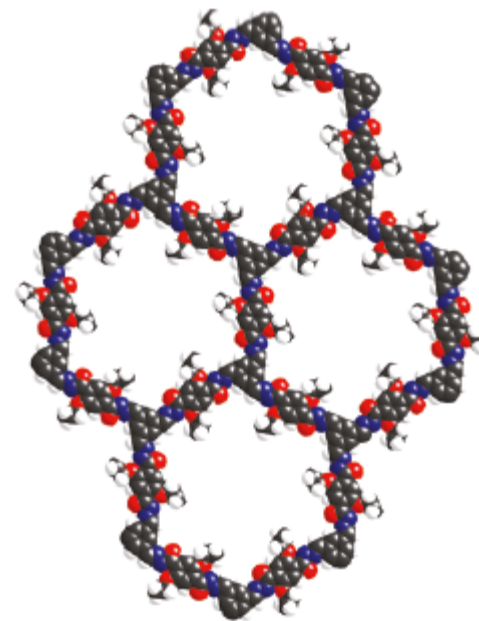
- Condensation of hydrazones forms very low density permanently microporous materials



9:1:1 mesitylene:
dioxane : acetic acid
120°C, 72h



COF-42

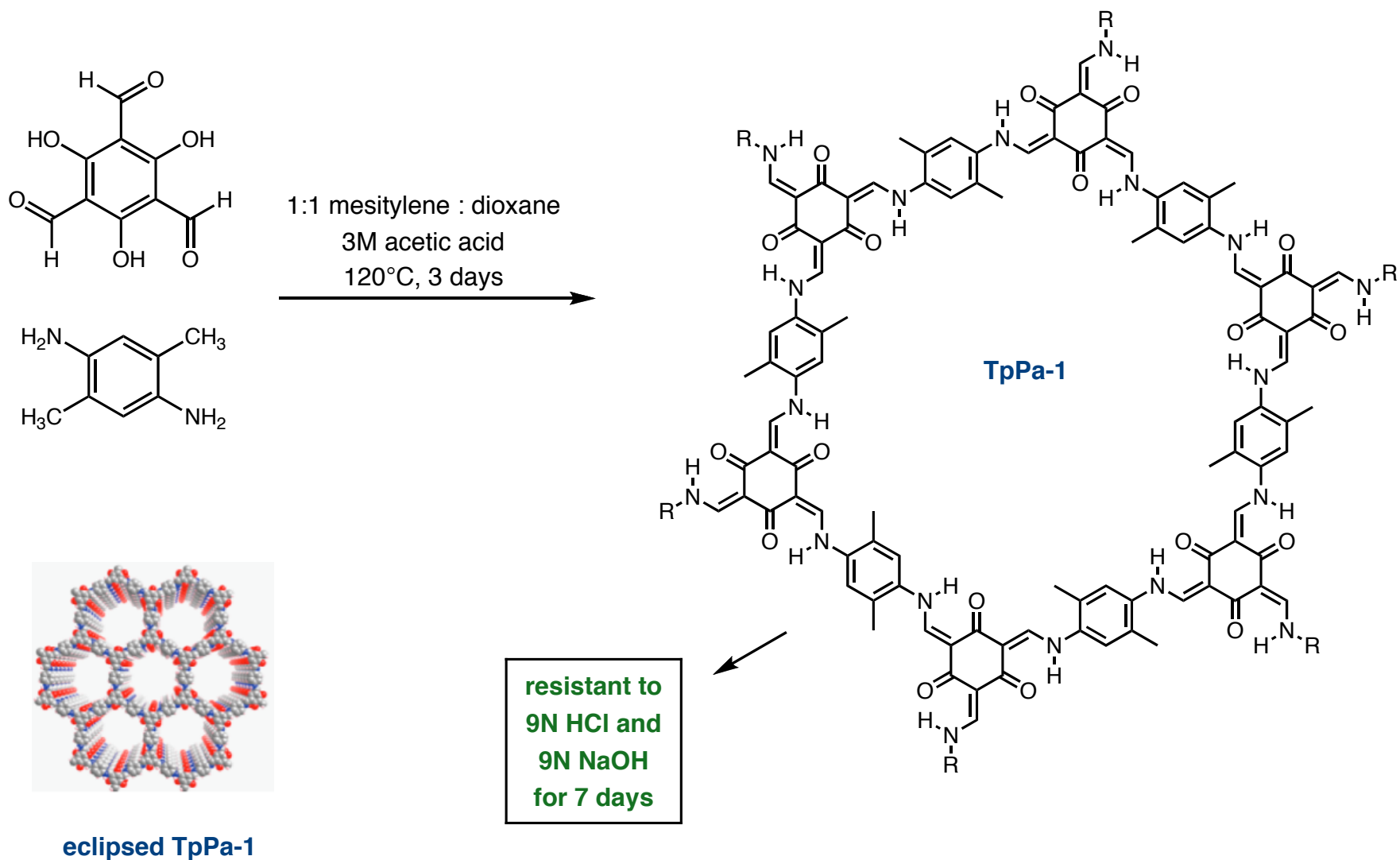


eclipsed COF-42

Hydrazone-Linked Covalent Organic Frameworks

Using Tautomerism to Increase Chemical Integrity

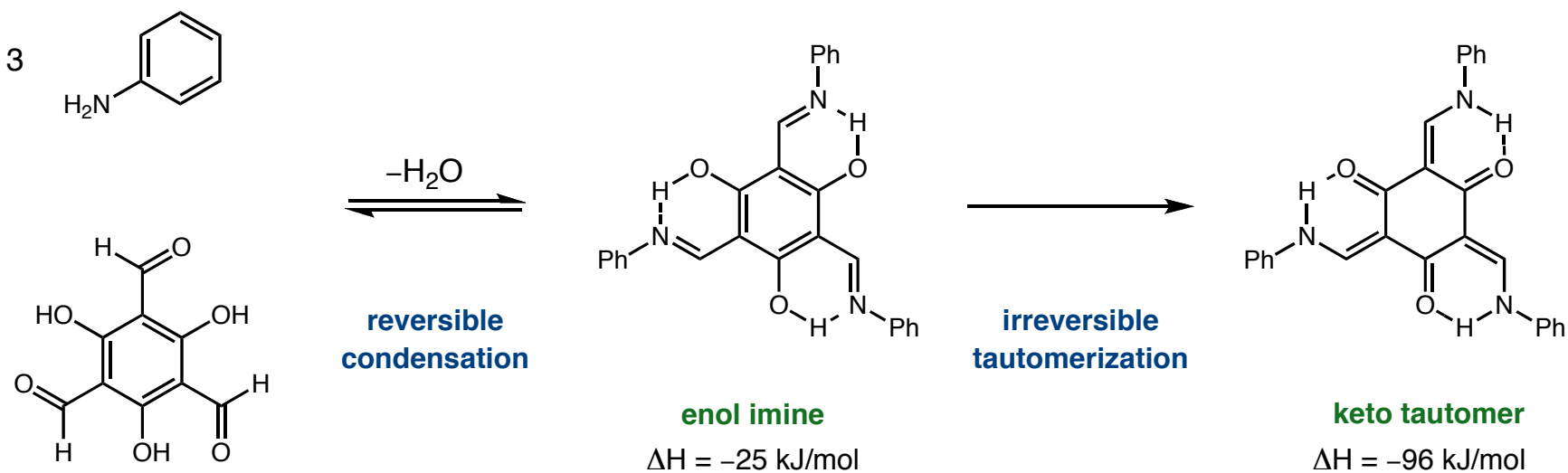
- Condensation of anilines with a special trialdehyde provides COF's resistant to both strong acid and base



Hydrazone-Linked Covalent Organic Frameworks

Using Tautomerism to Increase Chemical Integrity

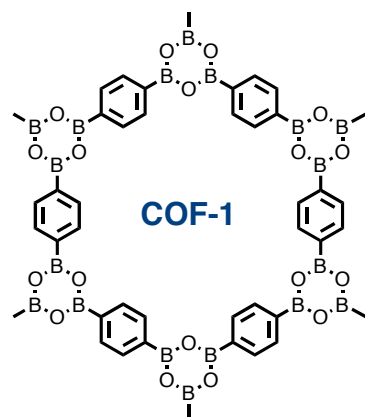
- Reversible condensation allows thermodynamic control, followed by irreversible tautomerization



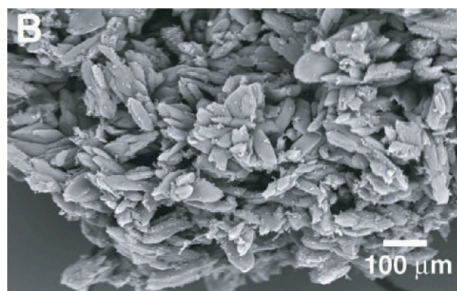
Covalent Organic Frameworks

Limitations of Crystallinity in COFs

- Limited reversibility of covalent bond formation means that most COFs are microcrystalline powders



≡

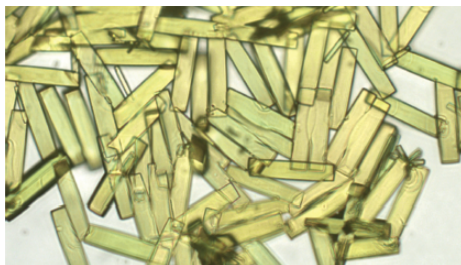


microcrystalline powder

Microcrystallinity

- mesoporosity
- processibility

- Single crystal materials are advantageous for x-ray analysis and extended properties



single crystals of a COF

Single Crystals

- X-ray crystallography
- long-range order

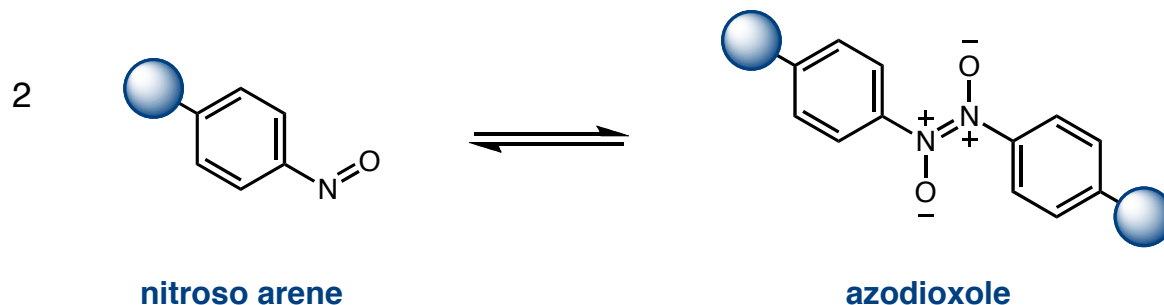
Beaudoin, D.; Maris, T.; Wuest, J. *Nat. Chem.* **2013**, *5*, 830.

Cote, A.; Benin, A. Ockwig, N.; O'Keefe, M.; Matzger, A.; Yaghi, O. *Science* **2005**, *310*, 1166.

Covalent Organic Frameworks

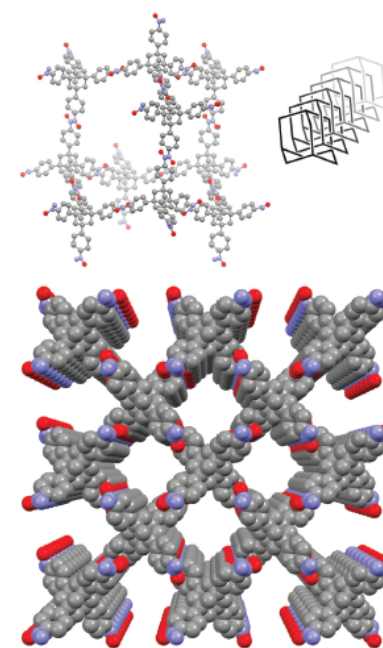
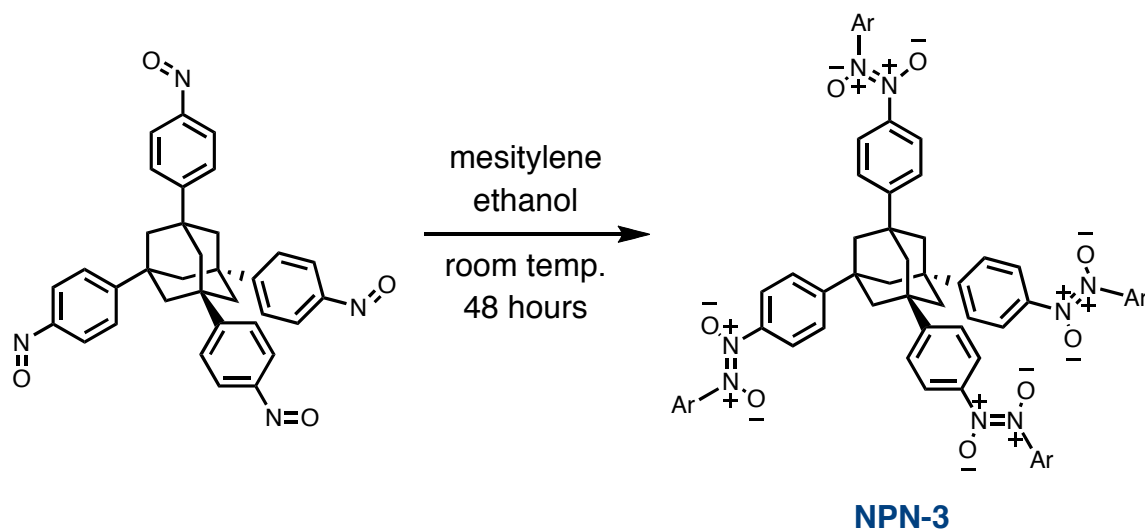
Limitations of Crystallinity in COFs

- The dimerization of nitroso compounds is thermally reversible, but not chemically degraded



$\Delta H = -20$ to -30 kcal/mol

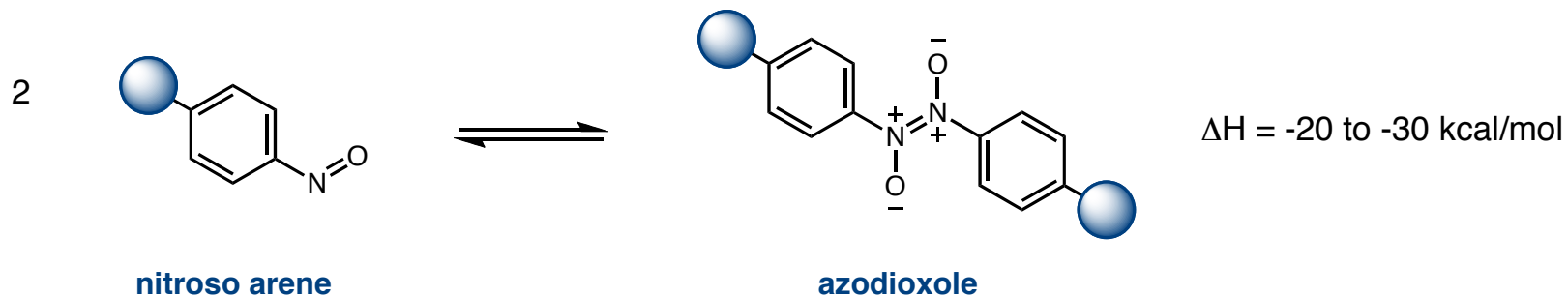
- Tetrahedral nitroso monomers generate resilient, covalent single crystals



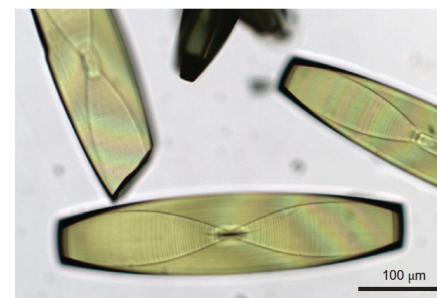
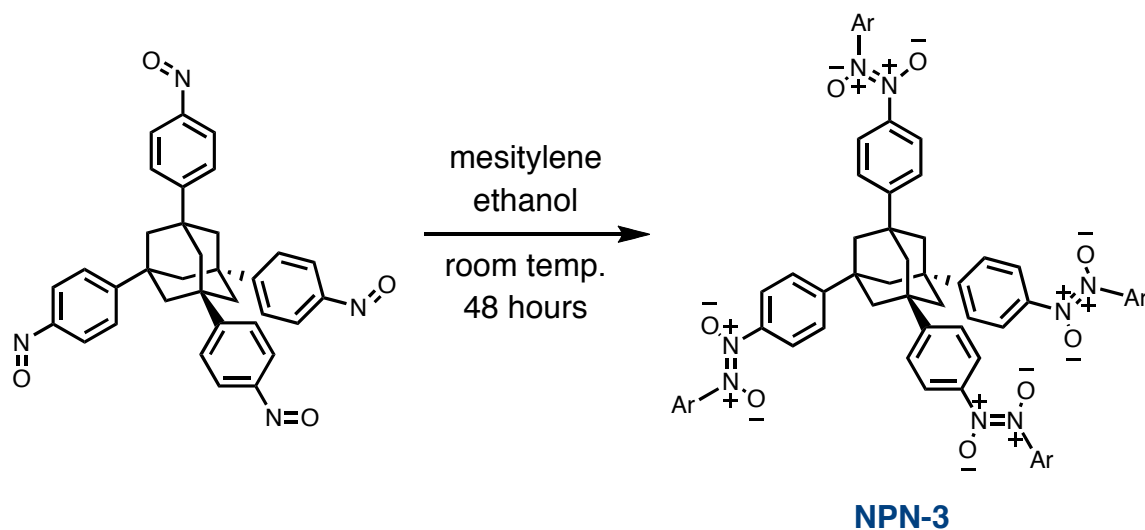
Covalent Organic Frameworks

Limitations of Crystallinity in COFs

- The dimerization of nitroso compounds is thermally reversible, but not chemically degraded

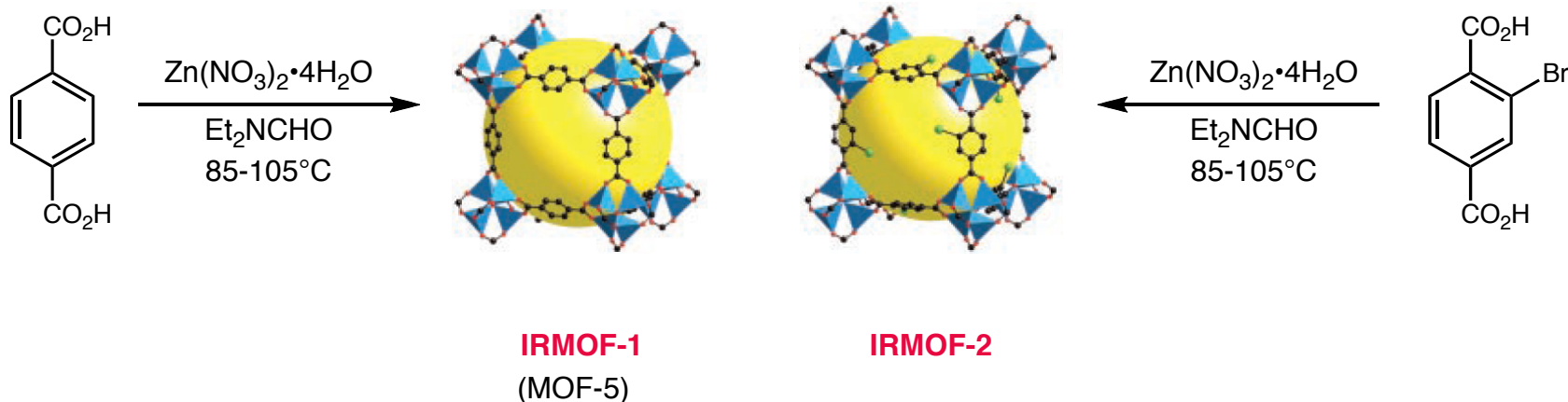


- Tetrahedral nitroso monomers generate resilient, covalent single crystals



Reticular Synthesis

- Two framework structures are said to be **isoreticular** if they are based on the same underlying topology
- Microporosity and modularity of MOF synthesis allow ready preparation of isoreticular polymers

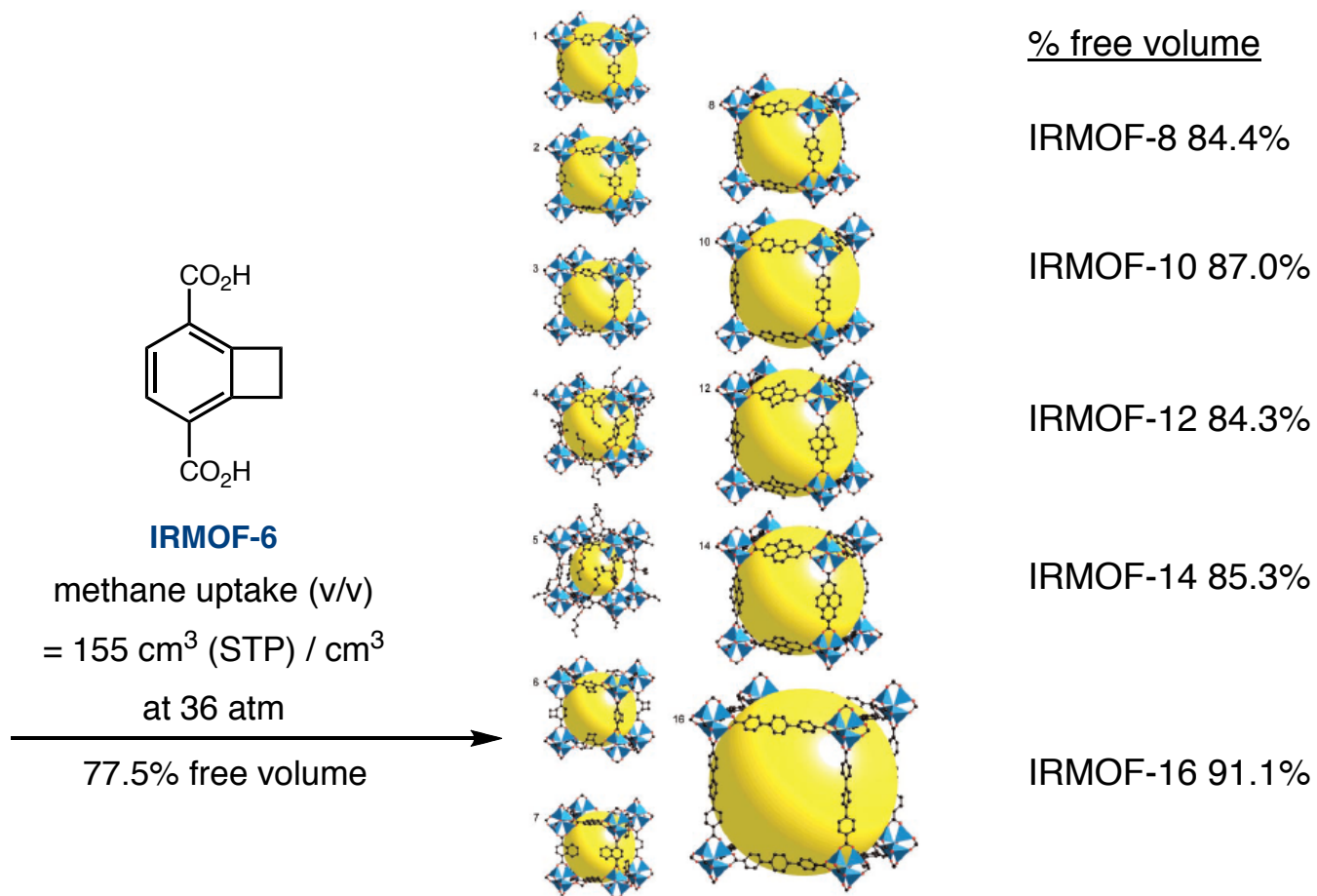


IRMOF = "isoreticular MOF"

The new strut adds functionality to previous void space without significantly altering the framework.

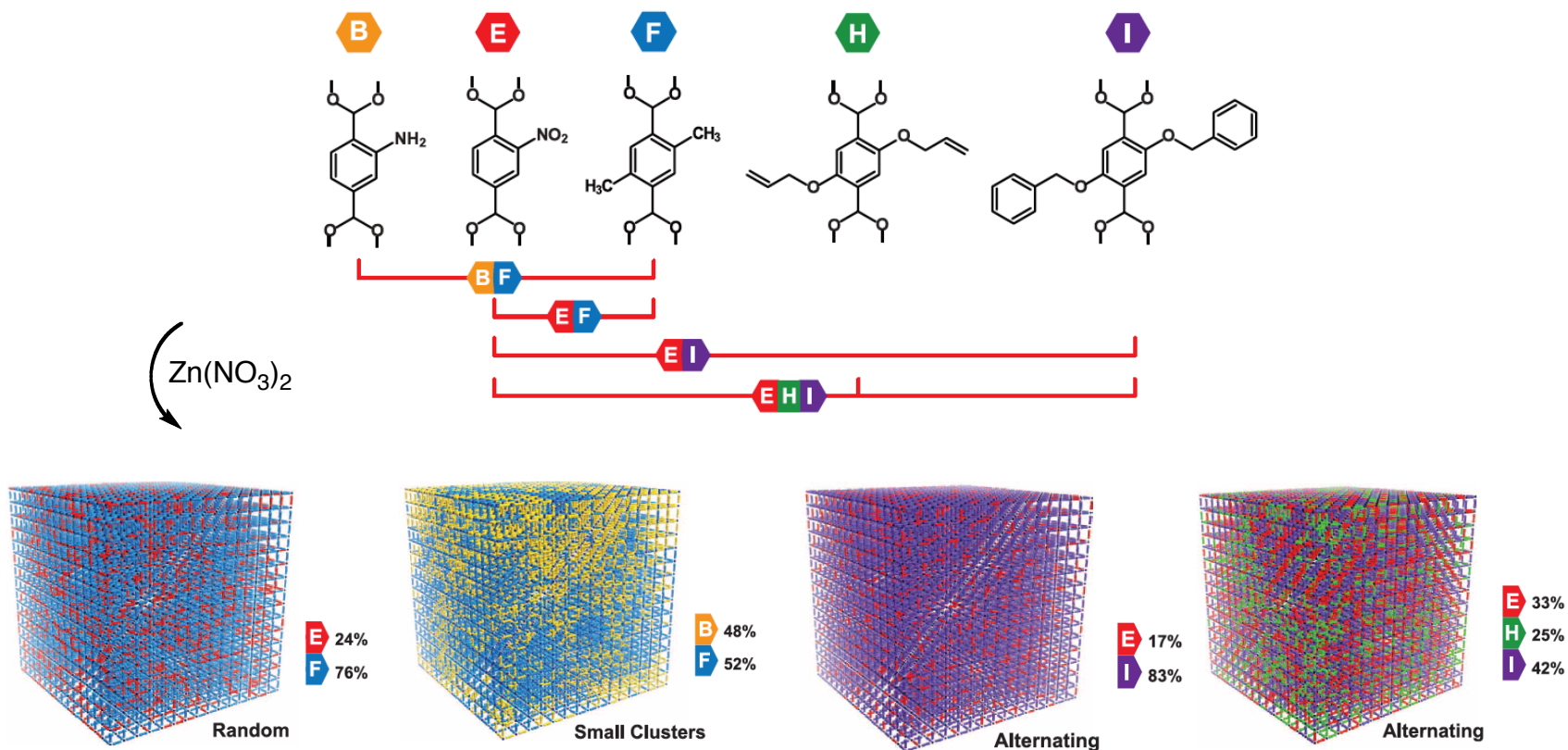
Reticular Synthesis

- Systematic variation of pore volume and polarity generates an isoreticular series for evaluation
- Adsorption of methane shown to be the most efficient in small, nonpolar pores



Multivariate Metal Organic Frameworks (MTV-MOF)

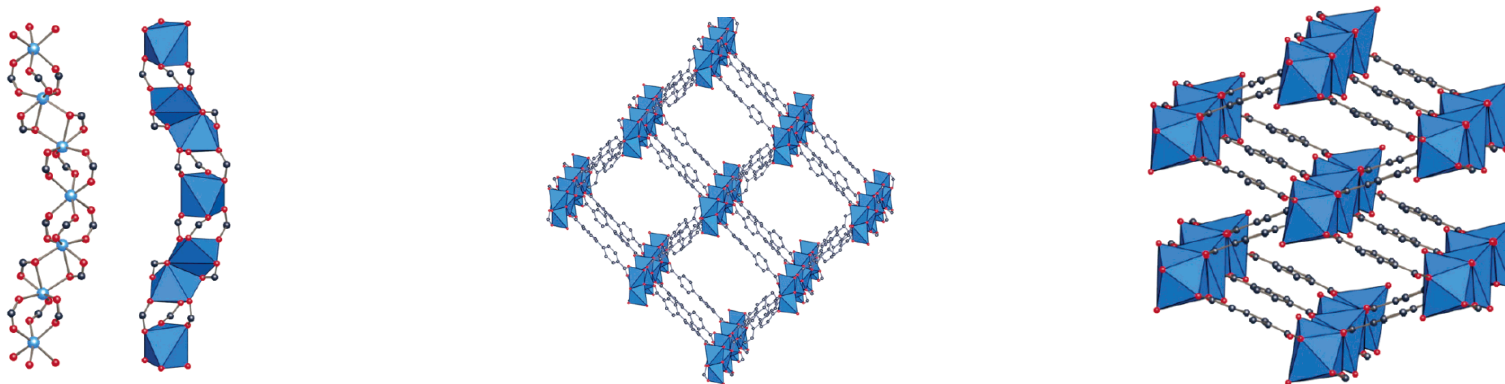
- Combination of monomers produce regular structures with a disordered functional group distribution



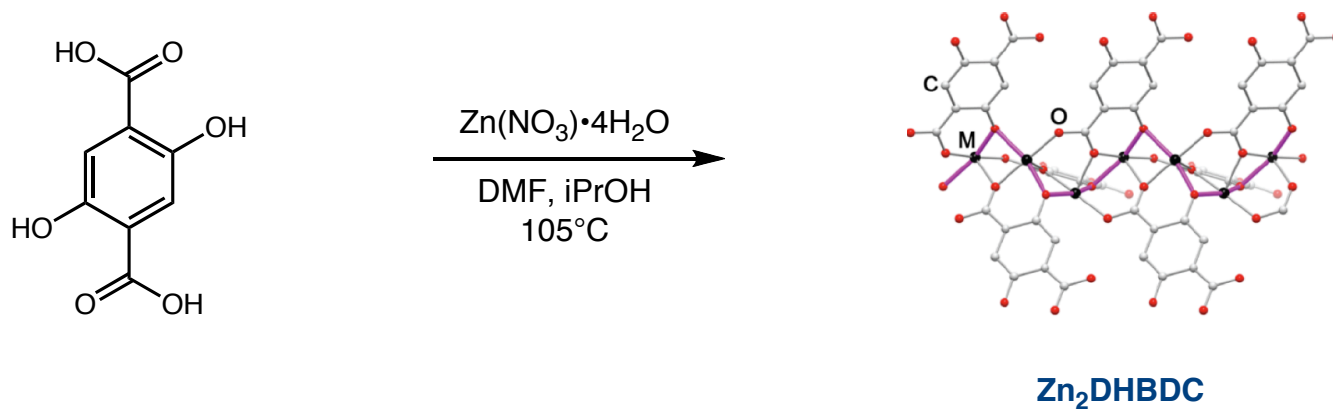
- Distribution type obtained by combination of REDOR-NMR and Monte Carlo simulations

One-Dimensional Secondary Building Units

- A variety of linear or rodlike SBUs are known, producing extended 1-dimensional channels

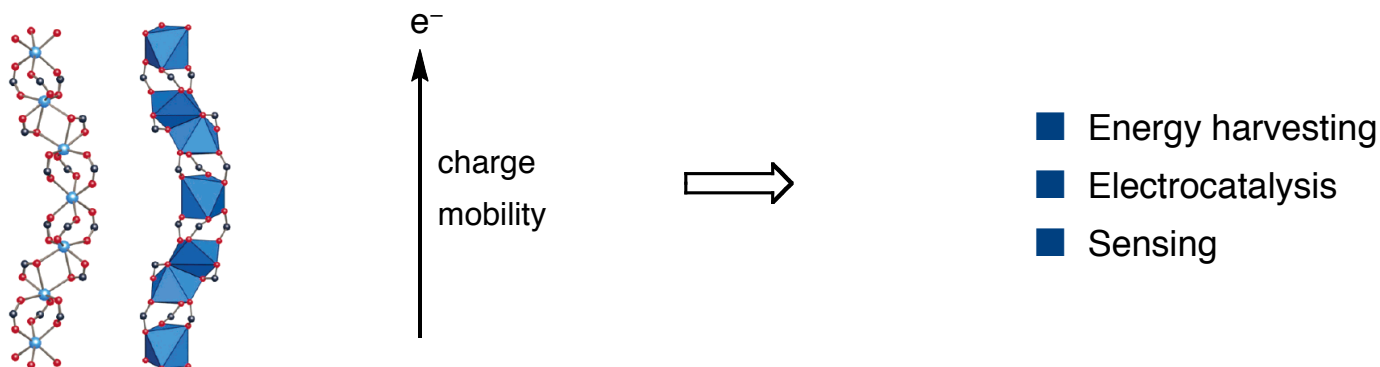


- Coordination of the tetradentate ligand 2,5-dihydroxybenzene-1,4-dicarboxylate (H_2DHBDC)

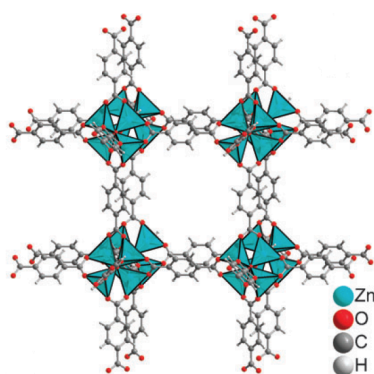


One-Dimensional Secondary Building Units

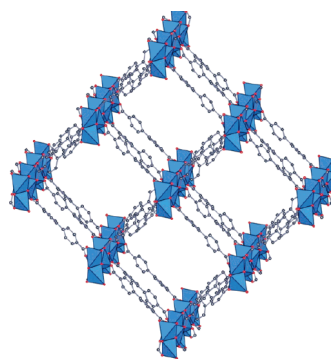
Potential Applications of Conductive MOFs



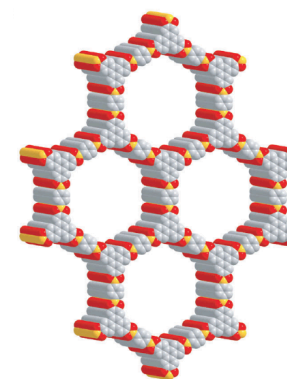
■ However, most COFs and most MOFs with either linear or node SBUs lack intrinsic conductivity



MOF-5



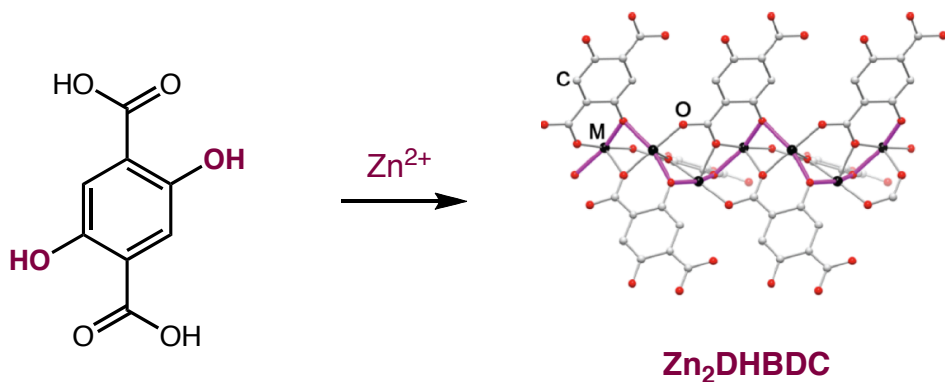
MOF-69A



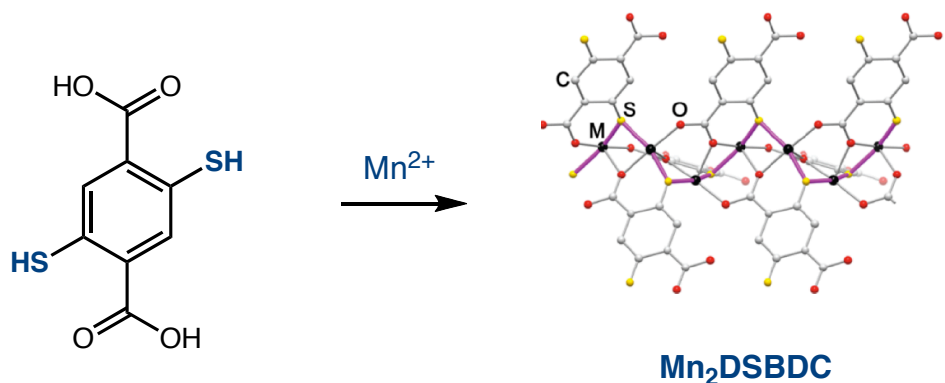
COF-5

Through-Bond Conductivity in 1D SBUs

Engineering Intrinsic Conductivity using Isoreticular Synthesis



- Infinite (–Zn–O–) chains
- Zn, O energy mismatch gives large band gap
- Electrical insulation

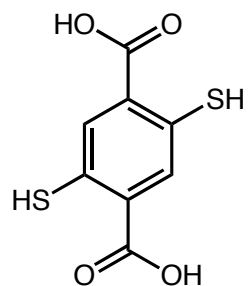


- Infinite (–Mn–S–) chains
- Mn, S energy match gives small band gap
- Charge mobility

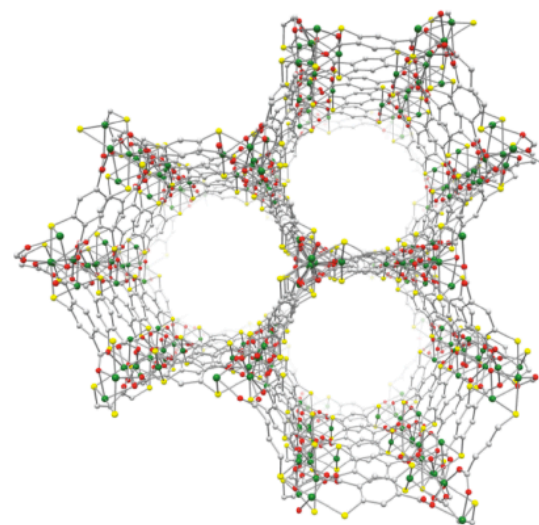
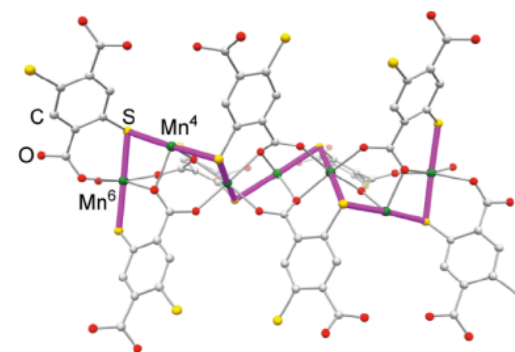
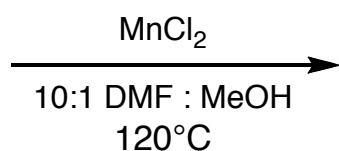
Isomorphous substitution provides the basis for electronic engineering of a MOF.

Through-Bond Conductivity in 1D SBUs

Engineering Intrinsic Conductivity using Isoreticular Synthesis



H₂DSBDC



Mn₂(DSBDC)(DMF)₂·0.2DMF

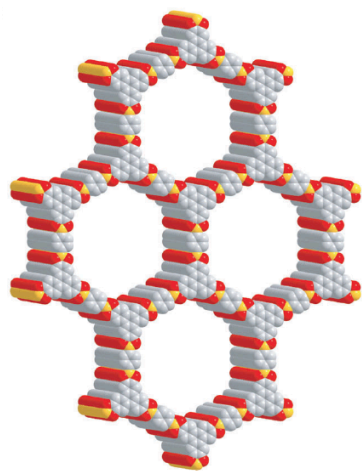
- Charge mobility comparable to that of organic polythiophenes
- Highest surface area known for a conductive MOF

Design of charge mobility provides materials with both high surface area and conductivity.

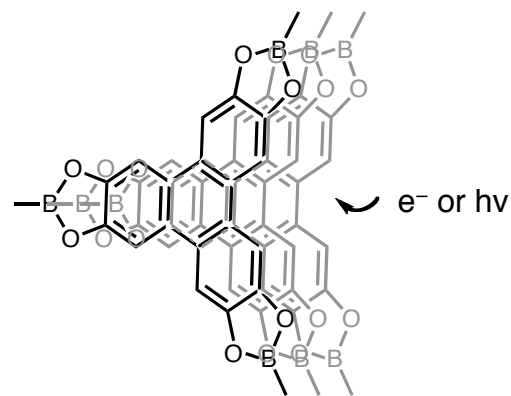
Through-Space Charge Mobility in 2D-COFs

Exploiting the Eclipsed Overlapping

- Regular 1D stacking of arene groups presents a tantalizing target for charge and exciton transport

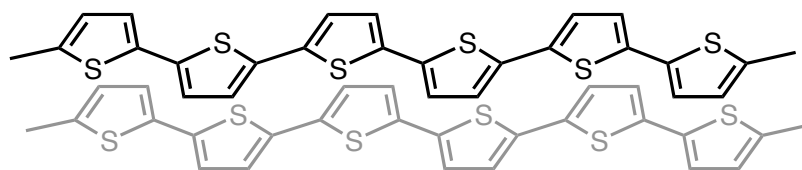


COF-5



3.46Å interlayer spacing

- Polythiophenes are well-known conducting donor polymers used in organic semiconductors

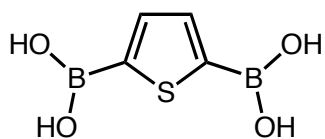


Reticular synthesis is proposed to engineer semiconductor properties into COFs

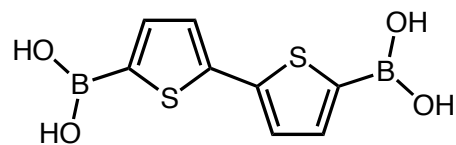
Through-Space Charge Mobility in 2D-COFs

Exploiting the Eclipsed Overlapping

- Poor crystallinity and irreproducibility are observed with linkers that are insufficiently linear and rigid

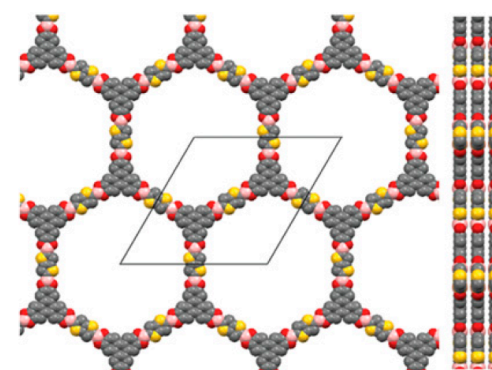
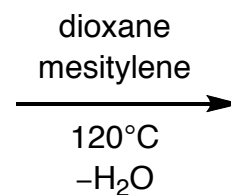
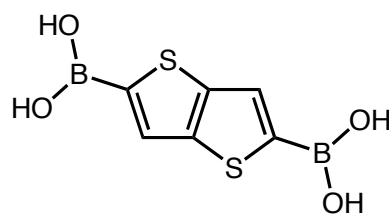
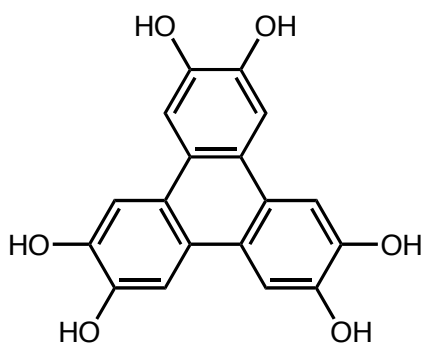


TCOF-2: rigid, but not linear



TCOF-3: linear, but not rigid

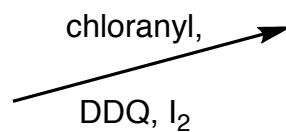
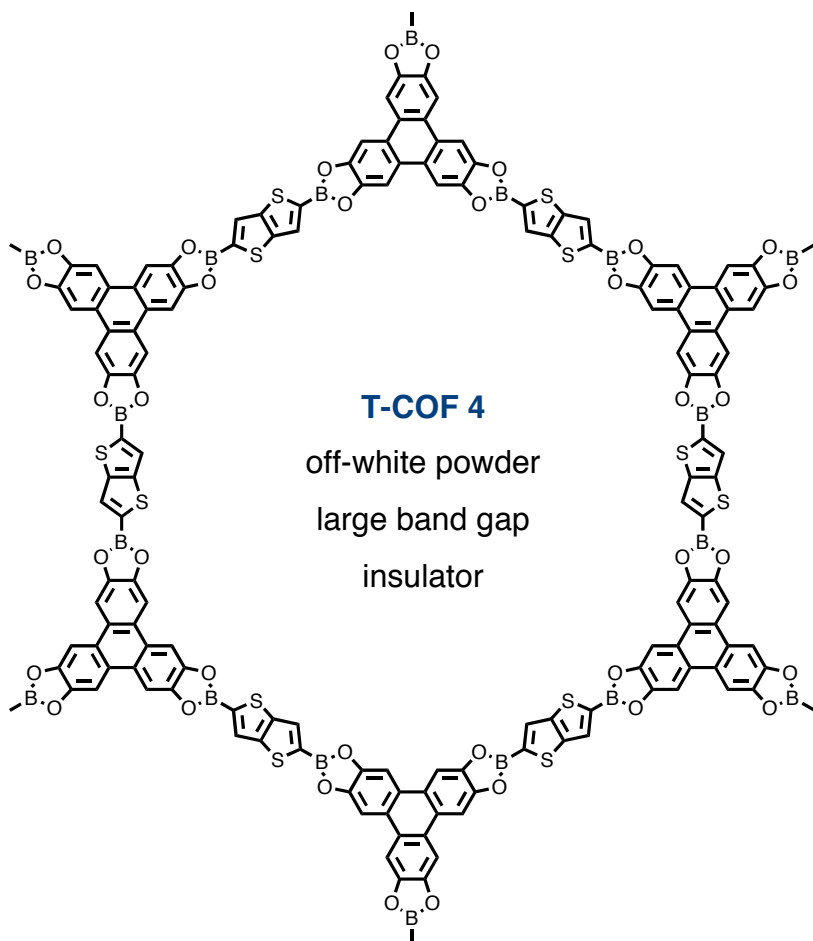
- A linker that is both linear and rigid produces a highly crystalline COF



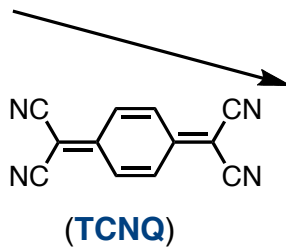
TCOF-4

Through-Space Charge Mobility in 2D-COFs

Oxidation required to generate a p-type semiconductor



loss of
crystallinity



TCNQCT-COF 4

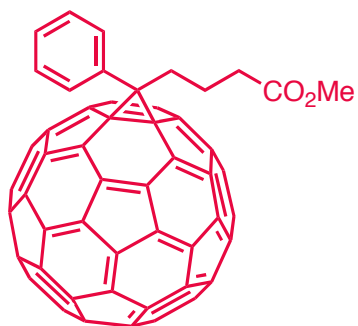
- Dark, charge-transfer complex
- Intercalation of acceptor between donor layers

The formation of a donor-acceptor complex suggests the possibility of photoconductivity in COFs.

Bulk Heterojunction Organic Solar Cells

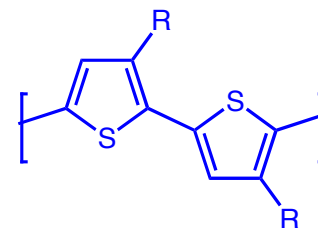
Phase Junction Morphology

Electron Acceptor:

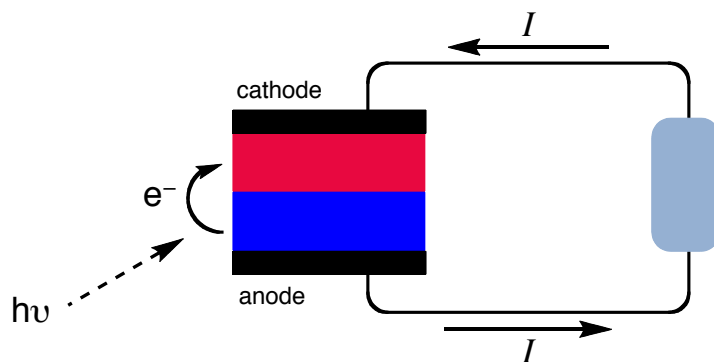


PCBM

Electron Donor:



a polythiophene



a simplified bulk heterojunction solar cell diagram

Layered junction:



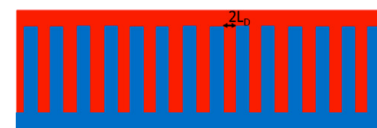
- Efficient transport
- Poor charge generation

Disordered junction:



- Inefficient transport
- Good charge generation

Nano-patterned:

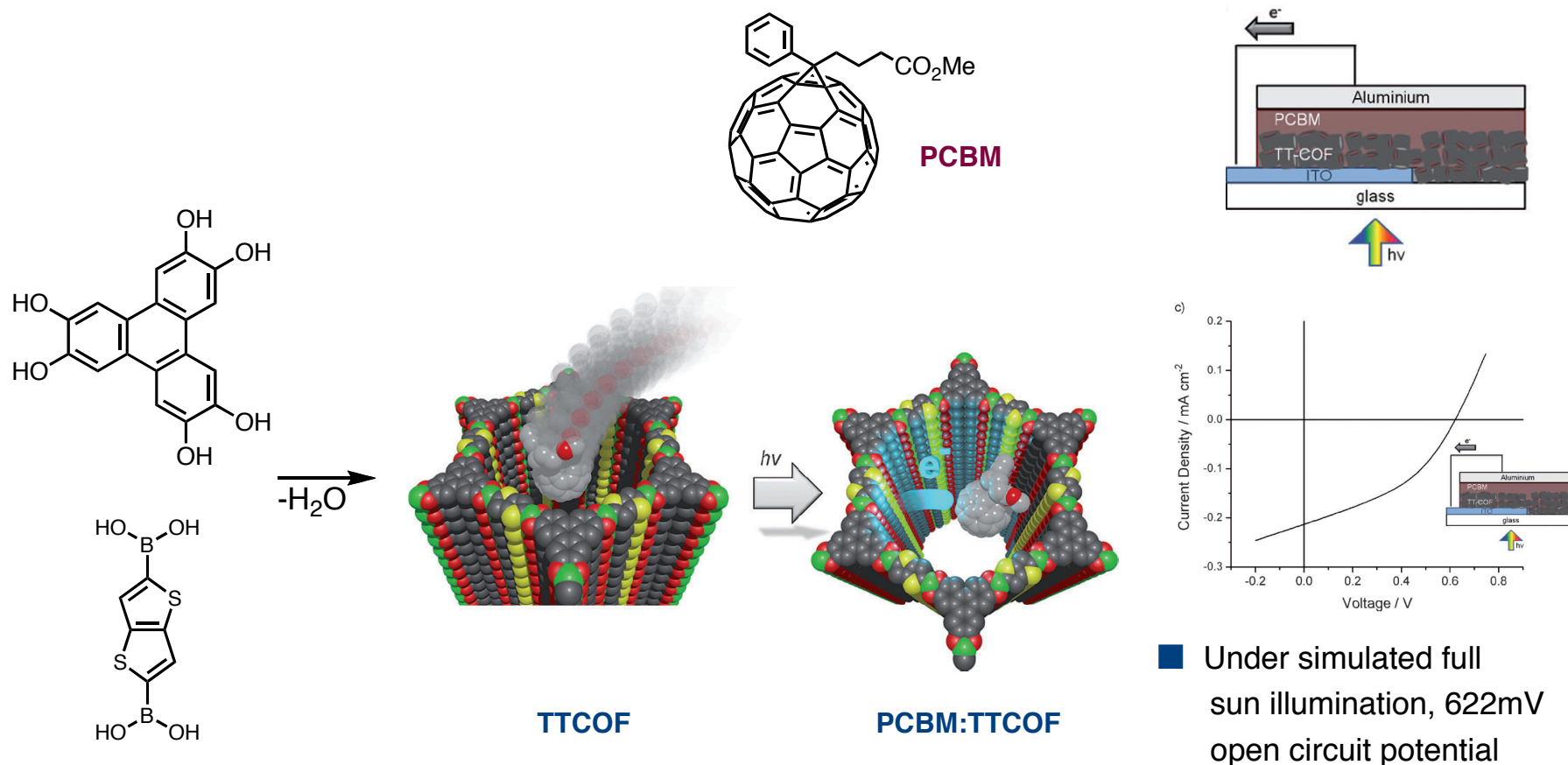


- Ideal morphology
- Challenging to make

Can permanent microporosity and long-range order in COFs be leveraged in organic heterojunctions?

Photocurrent in a Thienothiophene-Containing COF

Phase Junction Morphology

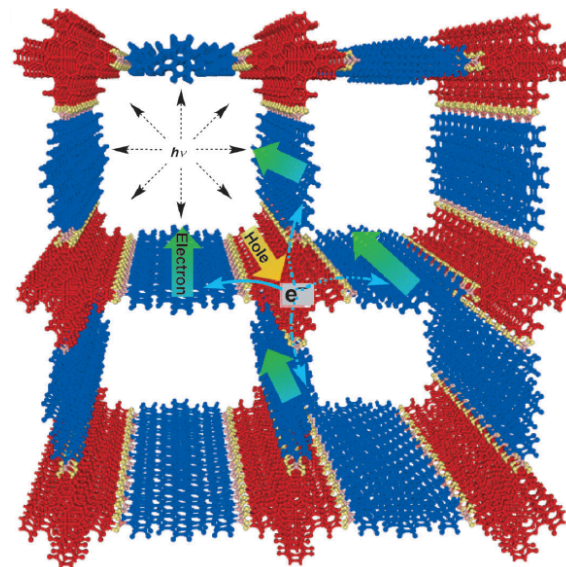
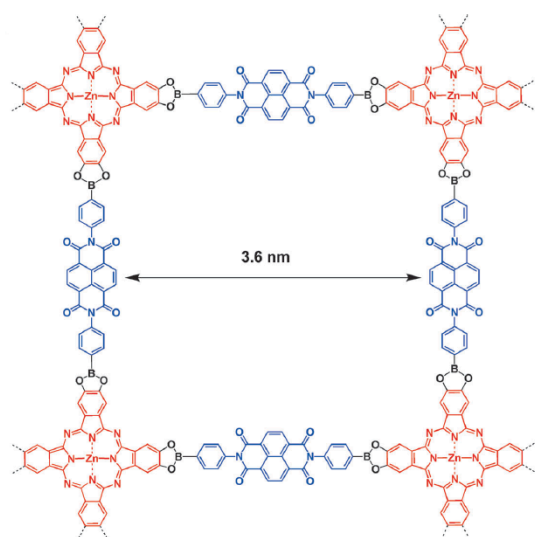


■ Channel pores of TTCOF are 3 nm, which is less than the 10-20 nm required for efficient charge transfer

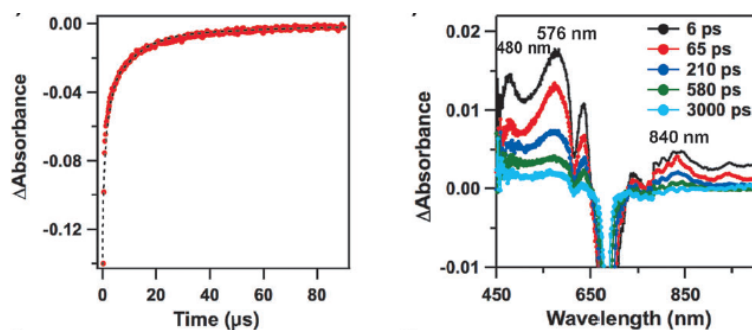
Incorporation of donors into backbone and acceptors into pores generates a functional BHJ cell.

Donor-Acceptor Covalent Organic Frameworks

Columnar Junctions as Model Systems for Charge Transfer



- Laser pulse experiments carried out at 430 nm, where efficient excitation takes place.

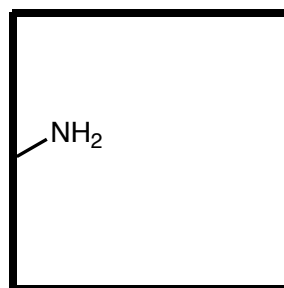
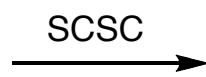
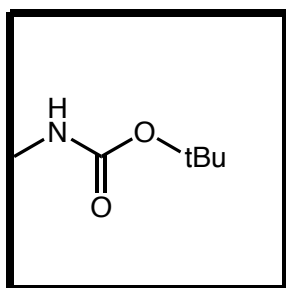


- Femtosecond transient spectroscopy: consistent with $\tau_{cs} = 10 \mu s$ and $ZnPc^{+} NDI^{-}$ ionization
- Time-resolved EPR: confirms ionization and a weak magnetic dipolar interaction between spins confirms charge delocalization

Efficient charge separation and rapid delocalization provide a model for bulk heterojunction design.

Post-Synthetic Modification

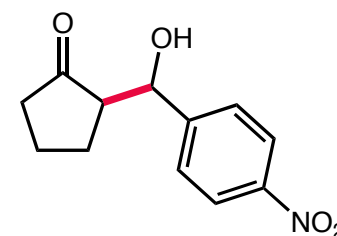
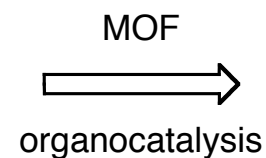
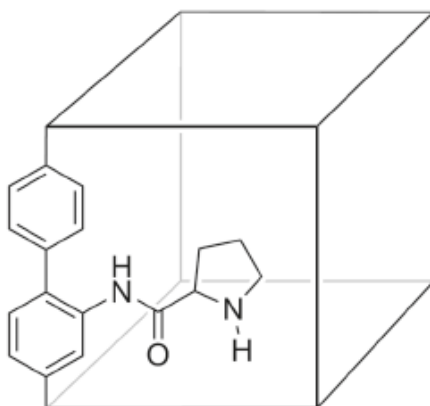
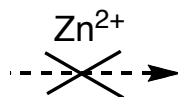
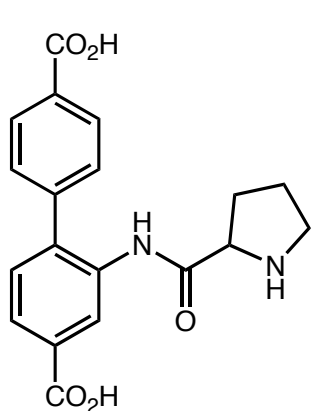
- Single crystal to single crystal (SCSC) reactions require high selectivity



Reaction must:

- Have high conversion
- Leave crystal framework intact

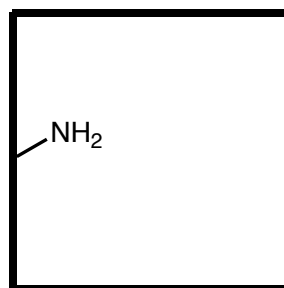
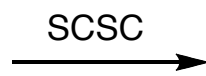
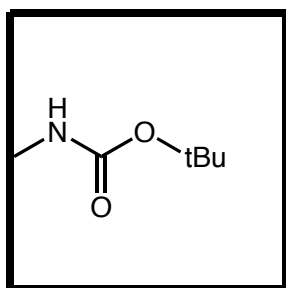
- Protecting groups are needed when desired functional groups are not compatible with crystallization



29% ee
3:1 dr

Post-Synthetic Modification

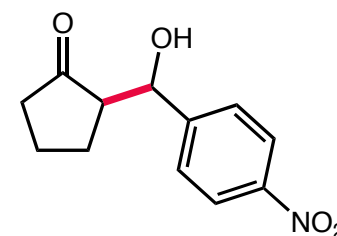
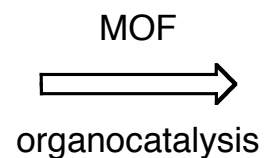
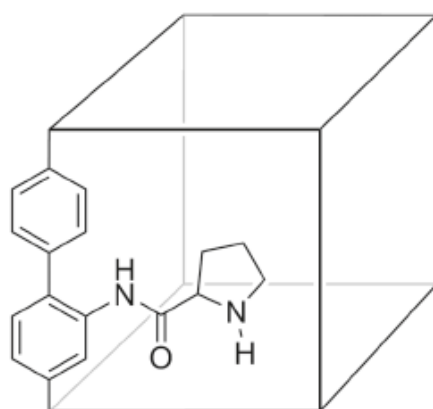
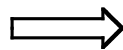
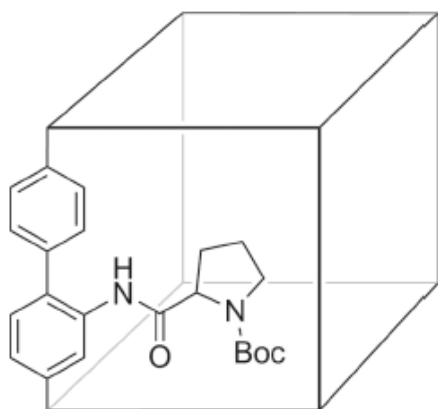
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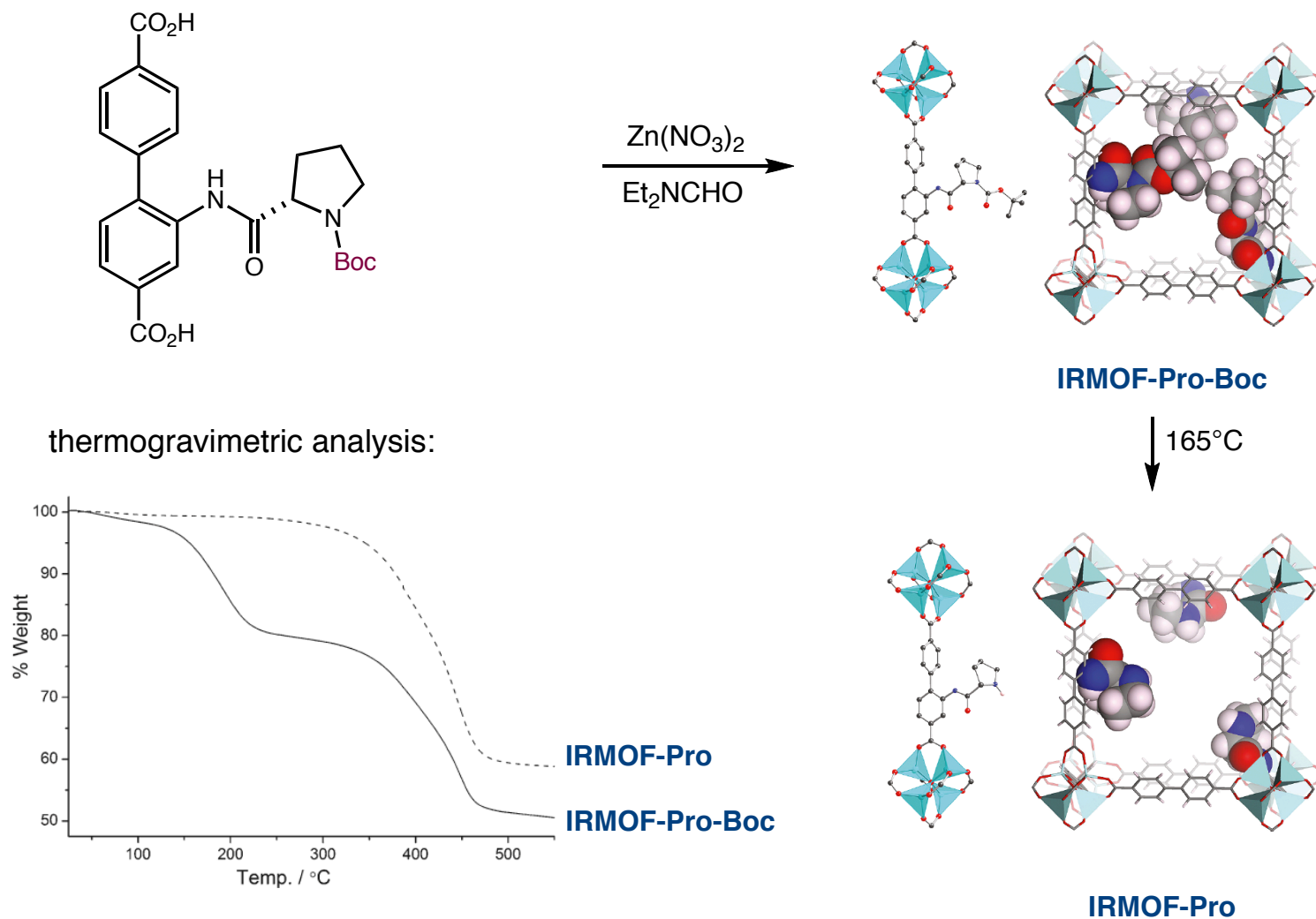
- Protecting groups are needed when desired functional groups are not compatible with crystallization



29% ee
3:1 dr

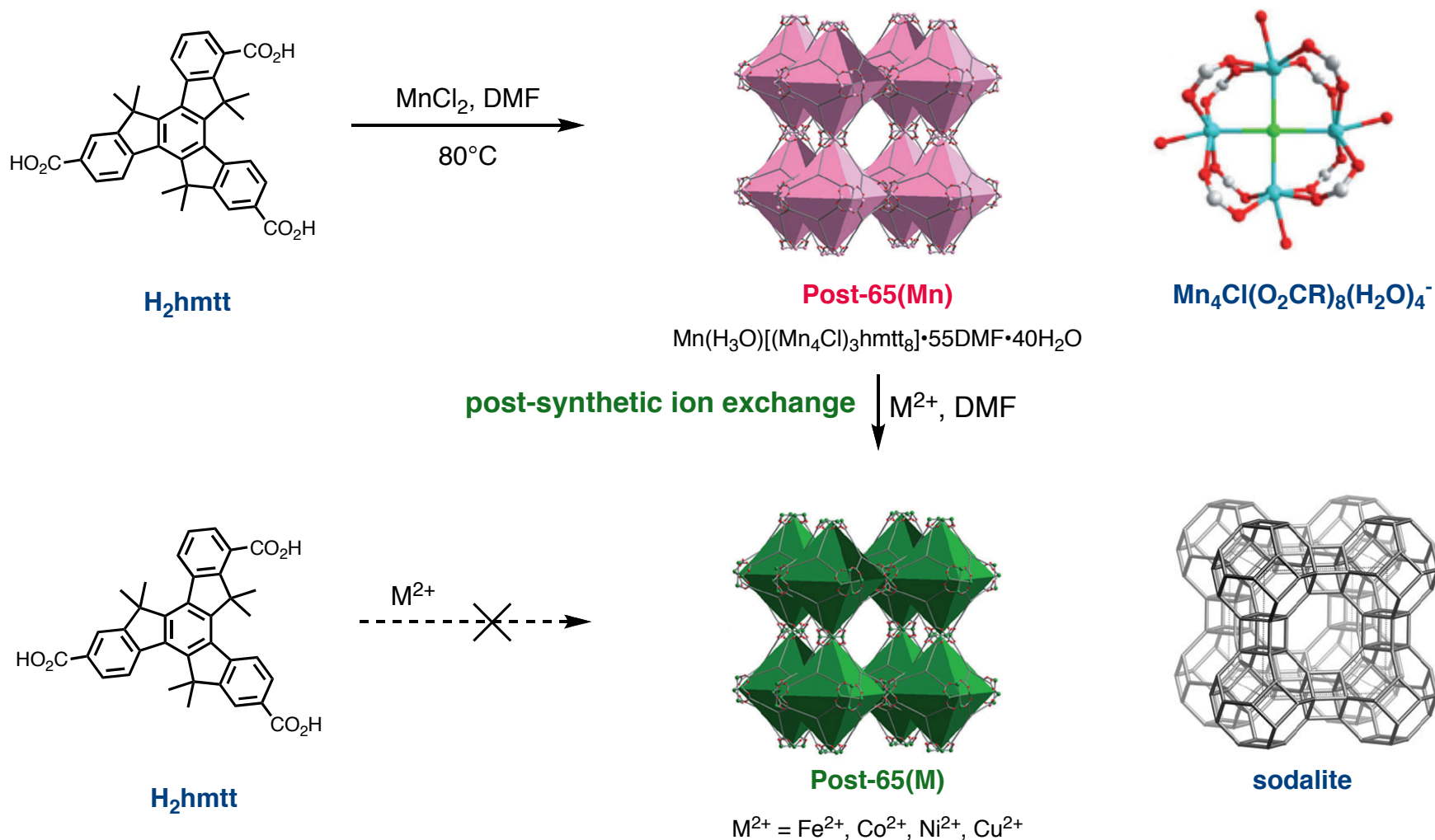
Boc Protection in the IRMOFs

- Reticular synthesis allows the preparation of a carbamate N-protected isorecticular MOF



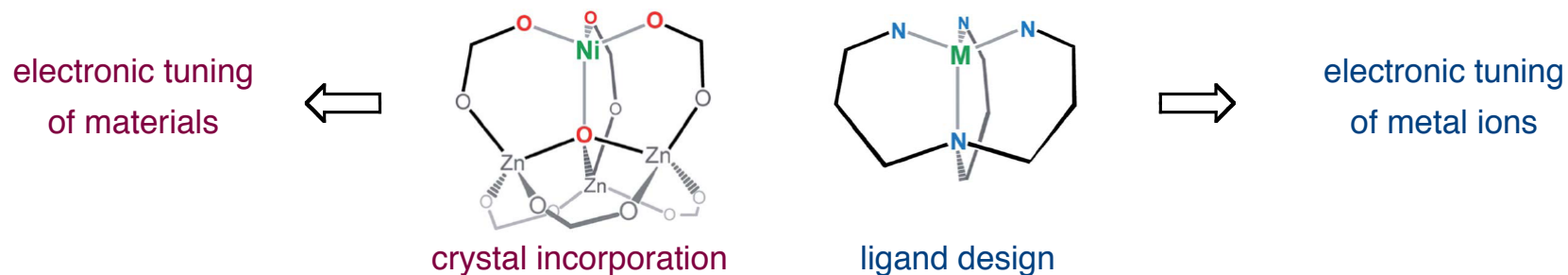
Post-Synthetic Ion Exchange in MOFs

- Exchange of metals allows preparation of MOFs that could not be crystallized directly

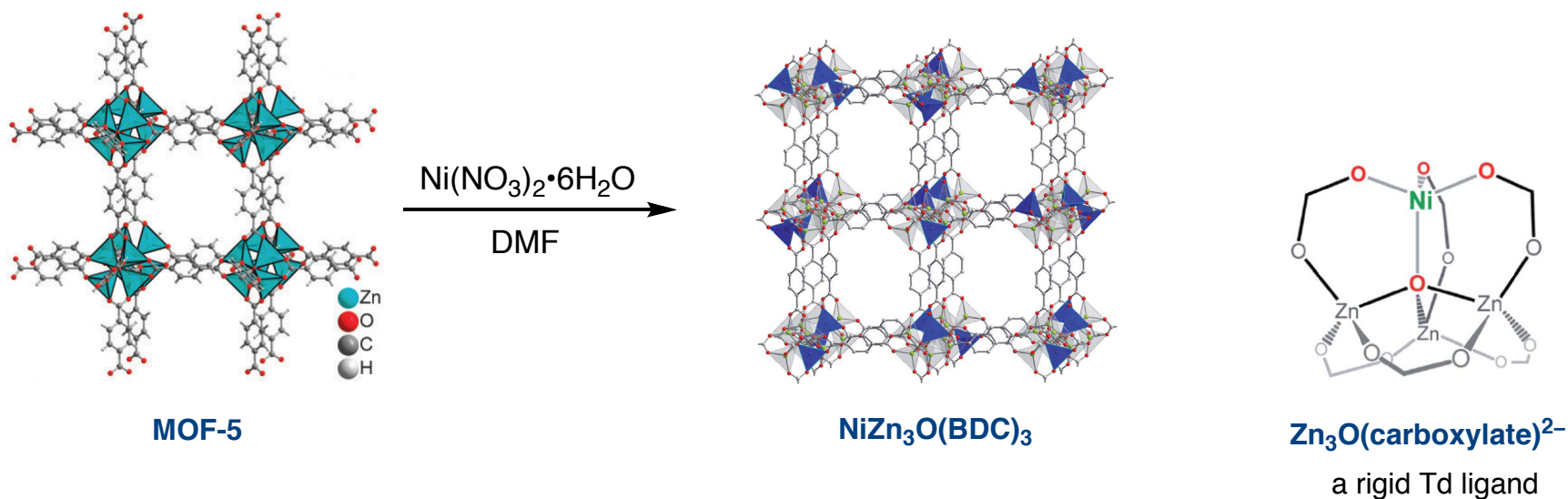


Post-Synthetic Ion Exchange in MOFs

- Control over metal ion coordination environment is a major objective of materials and inorganic chemistry

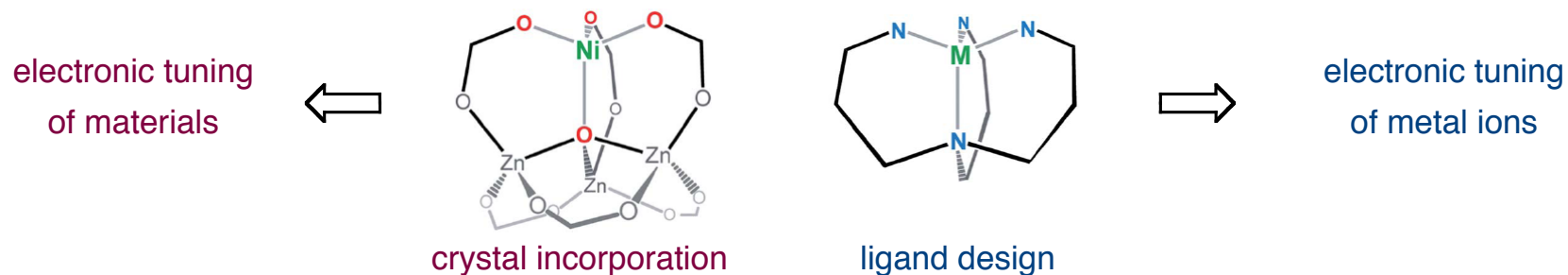


- MOF-5 was used as a rigid ligand environment to enforce an unfavored tetrahedral coordination of Ni^{2+}

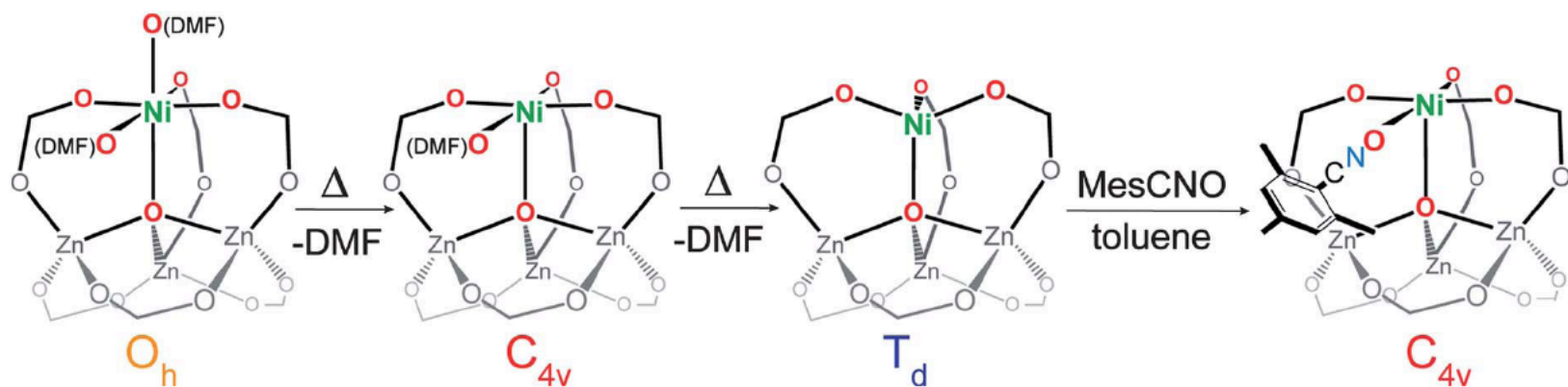


Post-Synthetic Ion Exchange in MOFs

- Control over metal ion coordination environment is a major objective of materials and inorganic chemistry



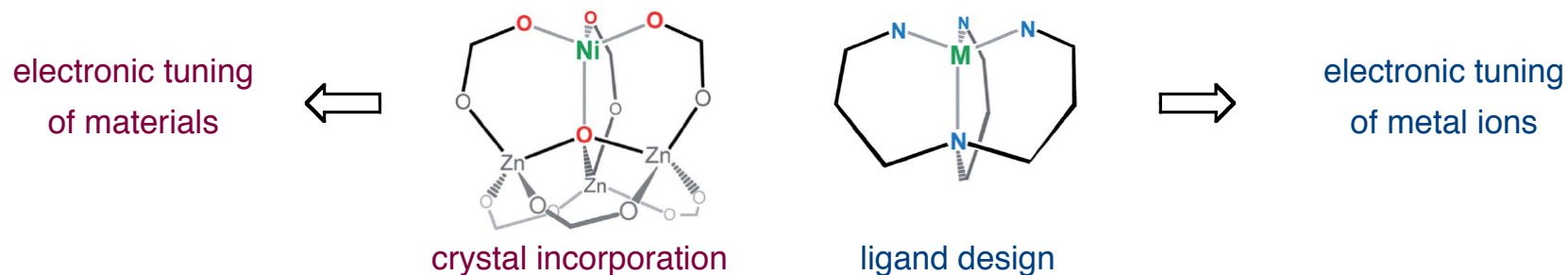
- IR/Vis diffuse reflectance spectroscopy was used to follow the intermediate coordination states of Ni²⁺



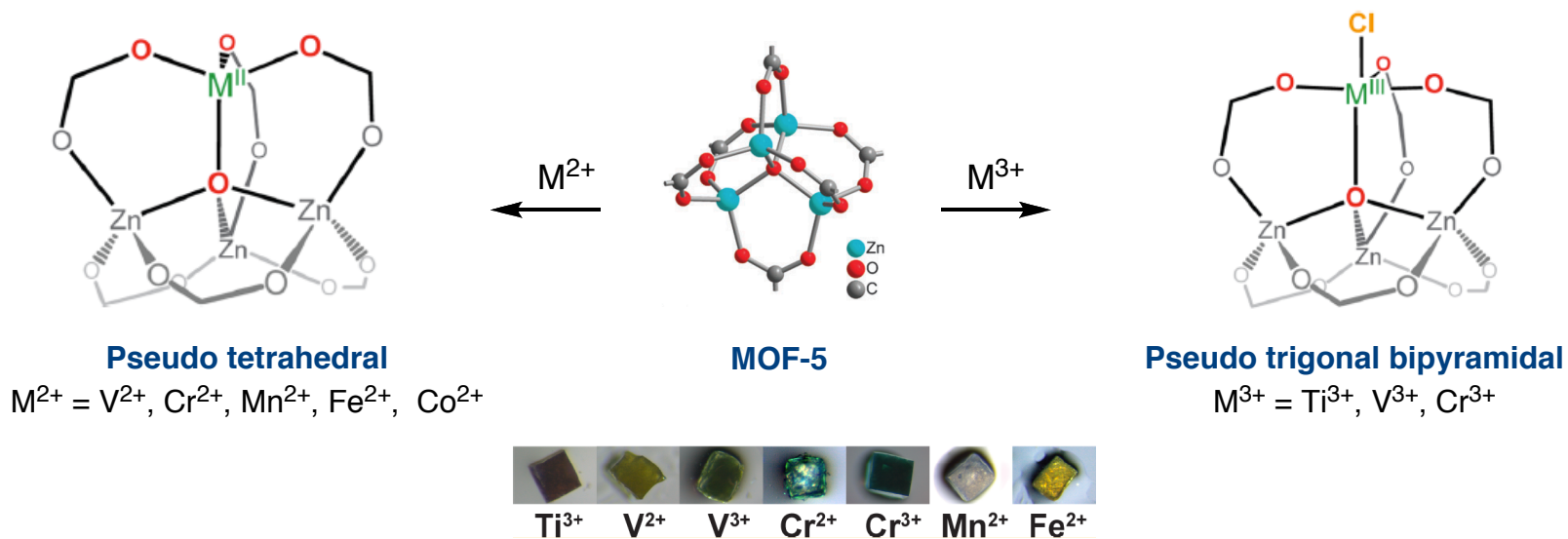
Single crystal to single crystal metal exchange preserves the desired ligand sphere.

Post-Synthetic Ion Exchange in MOFs

- Control over metal ion coordination environment is a major objective of materials and inorganic chemistry



- Exchange of a variety of low valent metals leads to previously unobserved coordination states

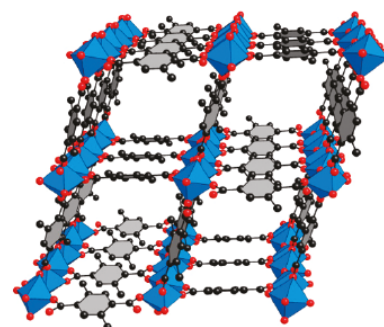
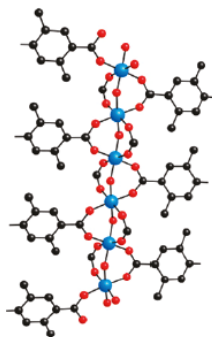


Oxidative Catalysis in MOFs

Evidence of Redox Cycling of SBU Metal Ions

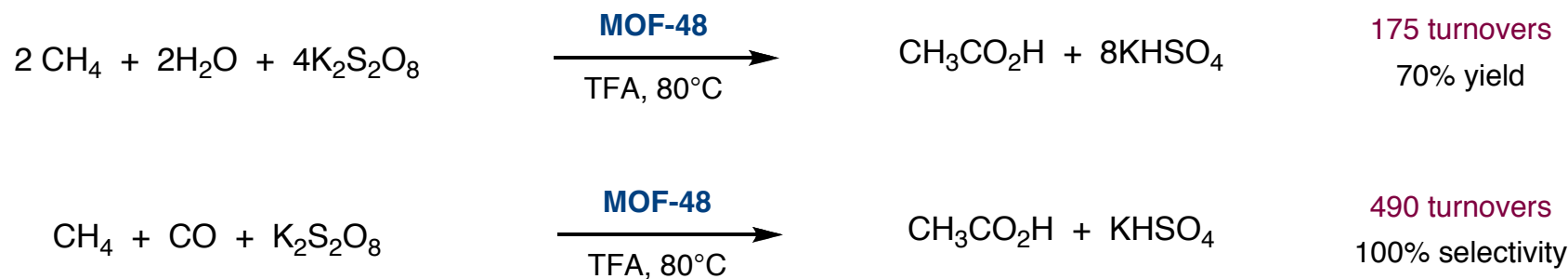
- Gas-phase oxidation of methane carried out in a V⁴⁺-containing MOFs

one-dimensional
V⁴⁺-containing
secondary
building unit



linear pore
structure of
MOF-48

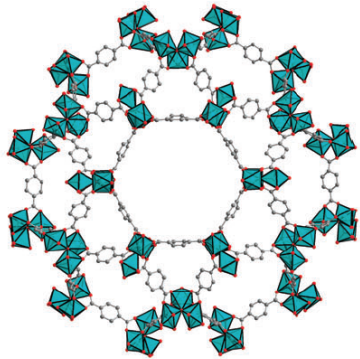
- High turnover and high selectivity for methane oxidation under mild conditions with MOF-48



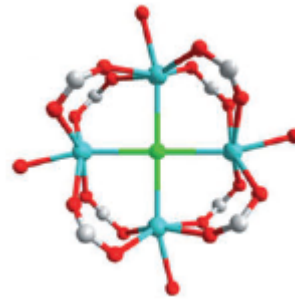
Single crystal to single crystal oxidation or reduction of MOFs could allow mechanistic insight.

Summary Slide

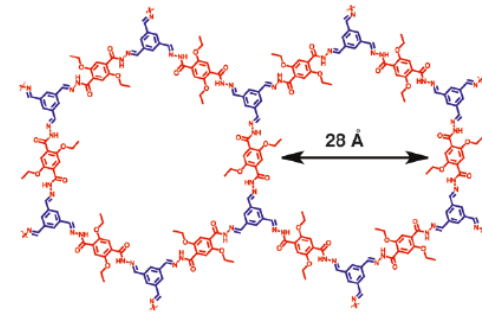
Metal-Organic Frameworks



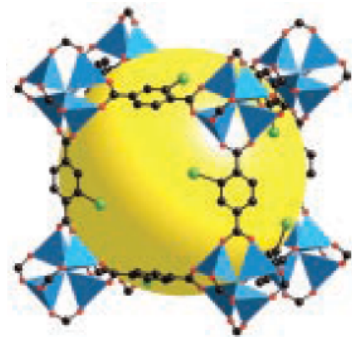
Secondary Building Unit



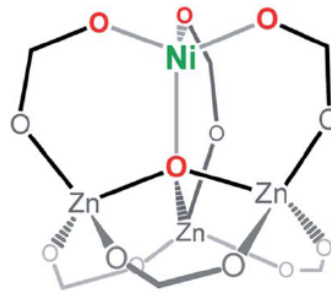
Covalent Organic Frameworks



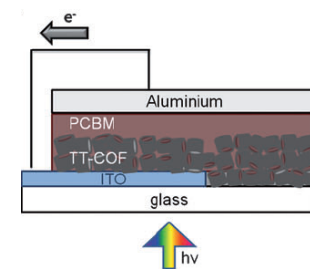
Reticular Synthesis



Post Synthetic Modification



Applications



The ability to design and analyze crystalline porous materials holds great potential for the customization of solid-state chemistry.