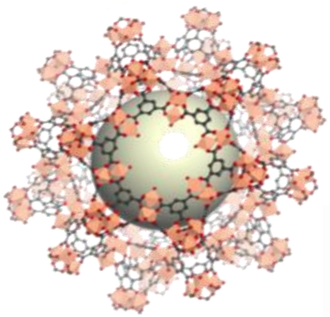
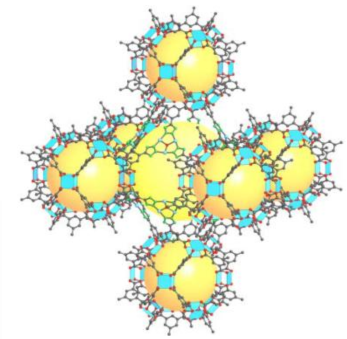
University of Crete
School of Sciences and Engineering
Department of Chemistry

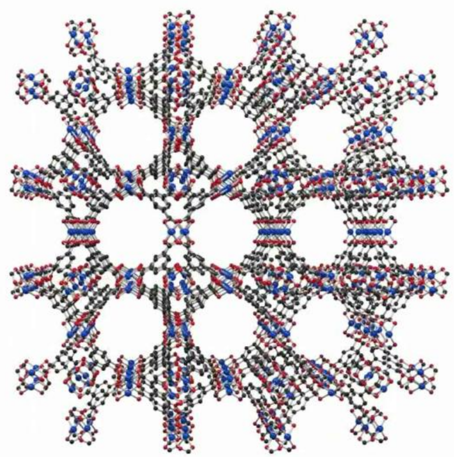
Reticular Chemistry:
MOF Design Strategies to Applications

(Molecular Precision in infinite 2D and 3D)





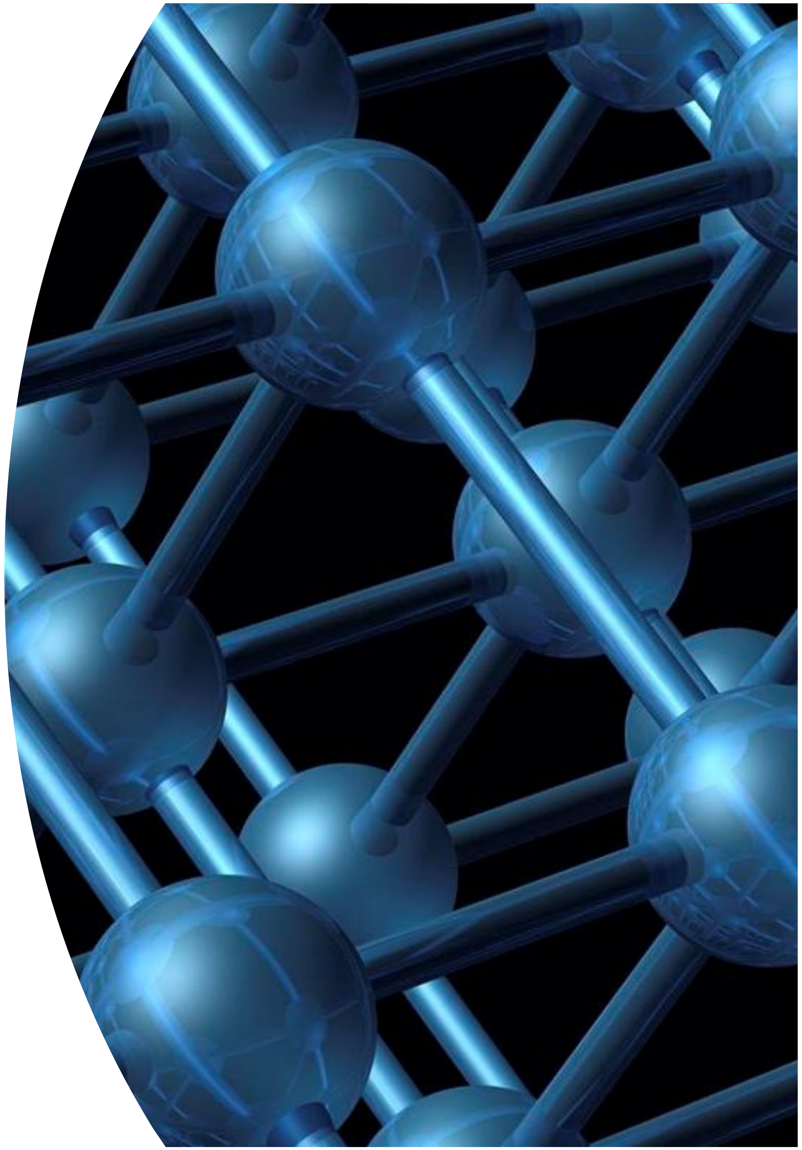
Konstantinos Froudas (1039)



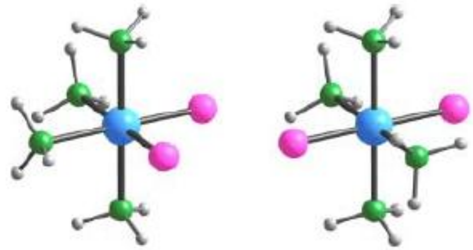
Supramolecular Chemistry

Heraklion, 4/5/2020

Contents



Emergence of MOFs



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(Nobel Prize,1993)

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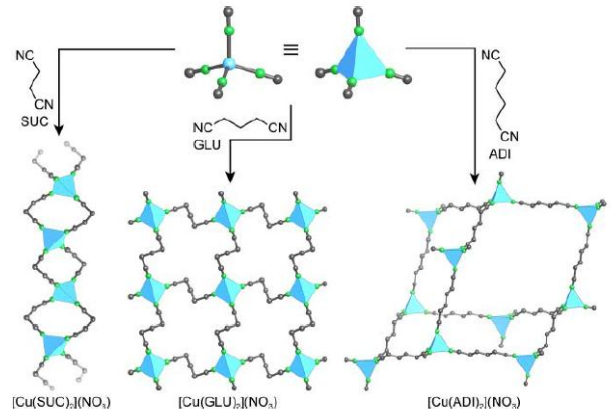
1893



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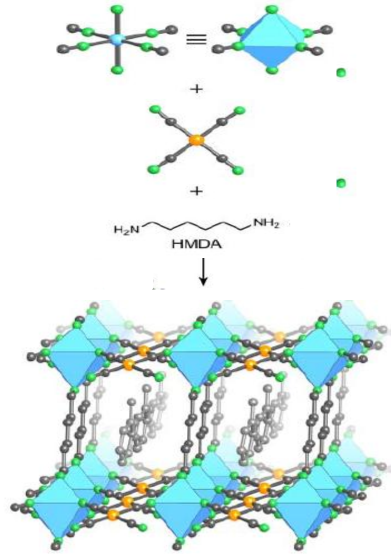

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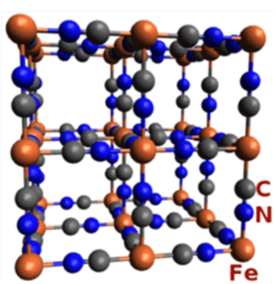
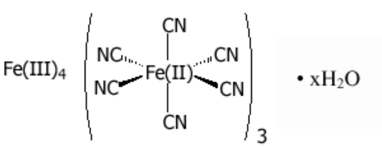
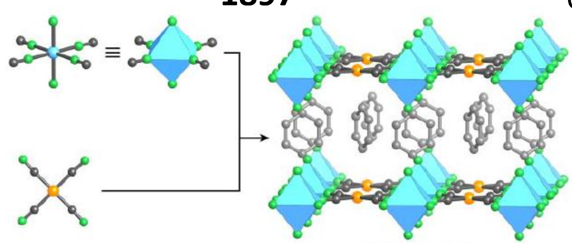




Prussian Blue

1897



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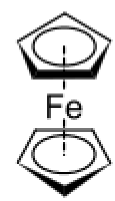
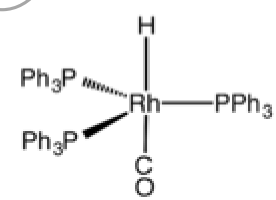
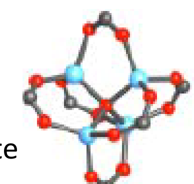




Development of the Organometallic Chemistry

1983-1984

Basic Zinc Acetate



Extended structures
Molecular chemistry

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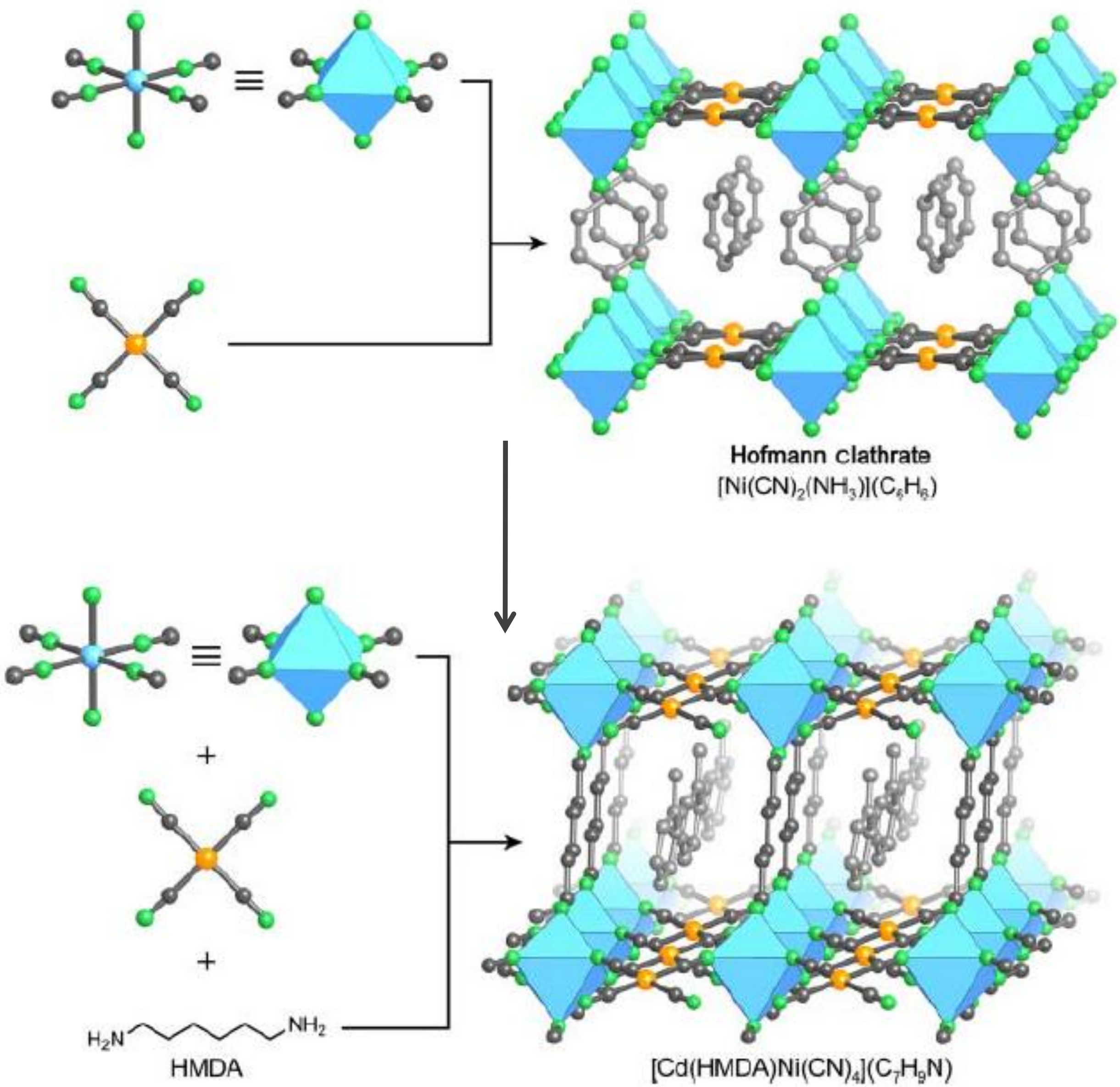

K. Hofmann and F. Kóspert, *Zeitschrift fór Anorganische Chemie,* **1897**, *15 (1), 204–207.*
S.-I. Nishikiori and T. Iwamoto, *Chemistry Letters,* **1984**, *13 (3): 319–322.*

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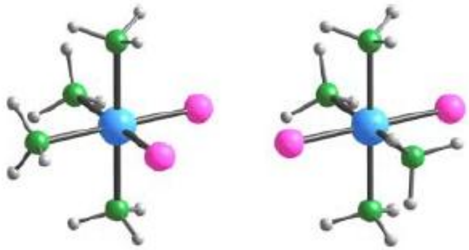

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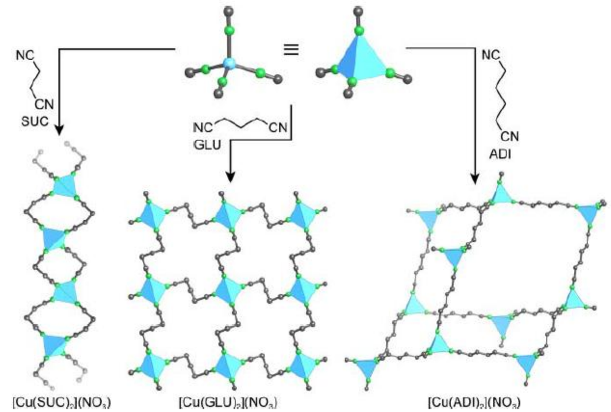

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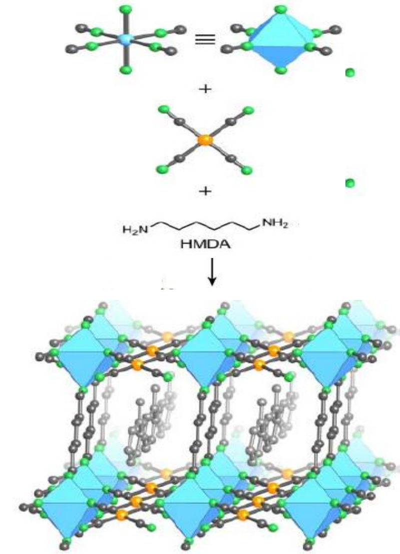

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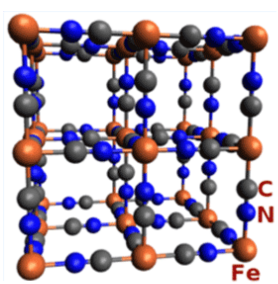

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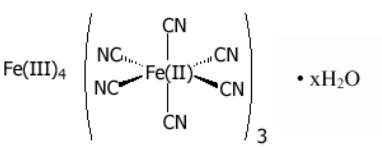

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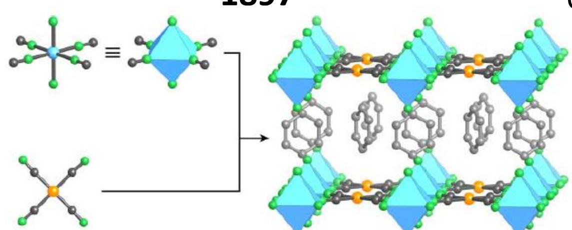

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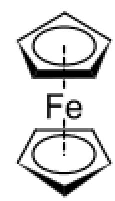

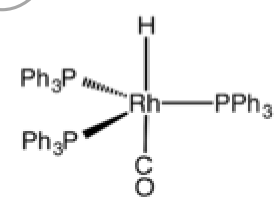

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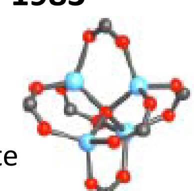

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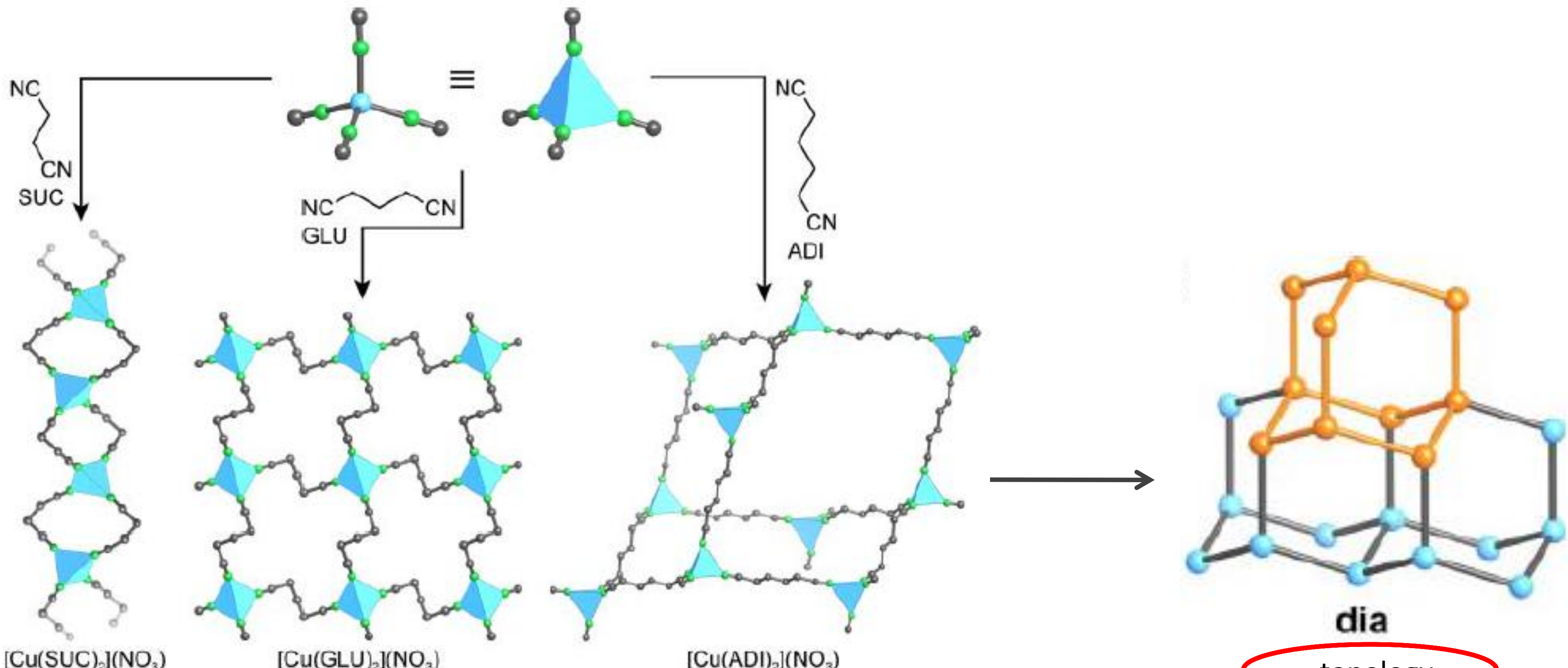
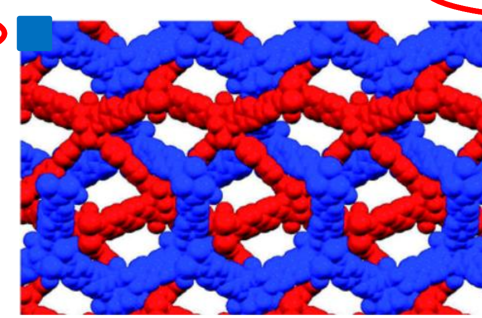
(Introduction of nitriles for the link of ions)



topology

interpenetrated



Y. Kinoshita, I. Matsubara and Y. Saito, *Bulletin of the Chemical Society of Japan*, **1959**, 32(7) 741–747.

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A. Wells, Acta Crystallographica, **1954**, 7 (8–9): 535–544.

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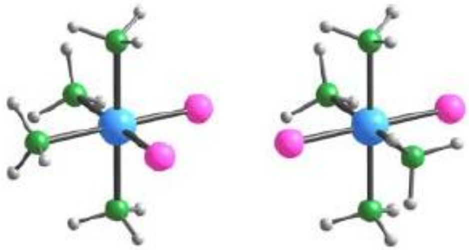

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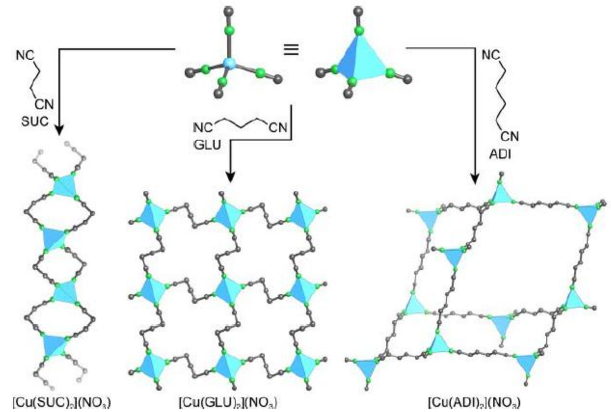

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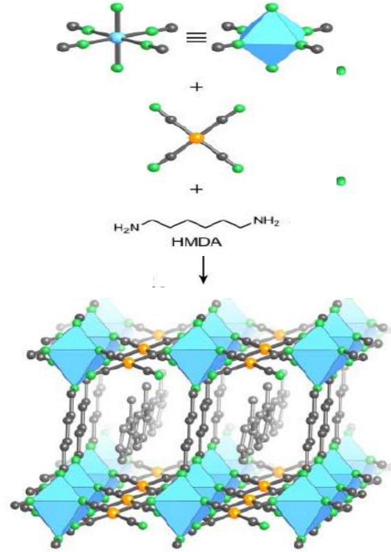

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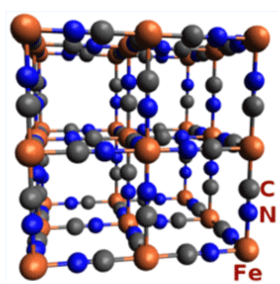

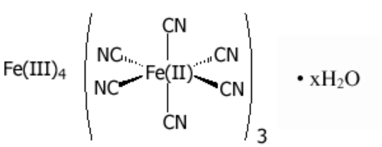

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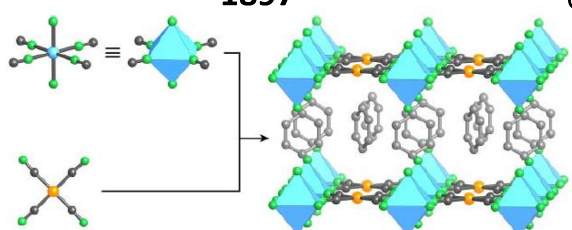

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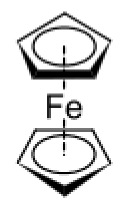

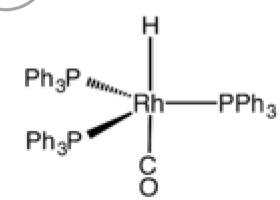

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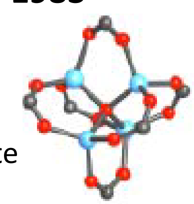

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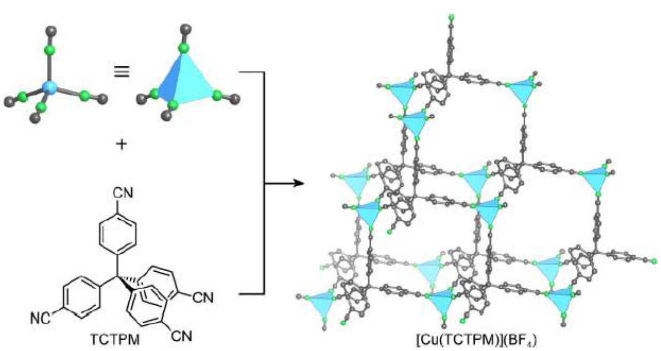
Design of coordination networks (Robson & Hoskins)



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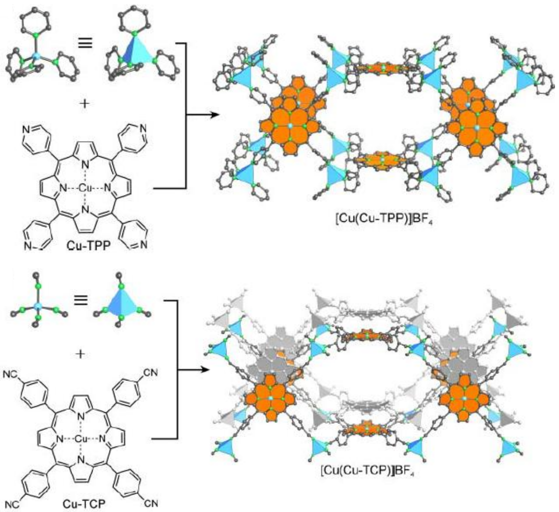

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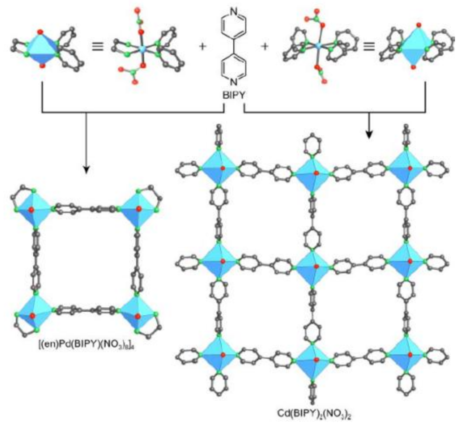

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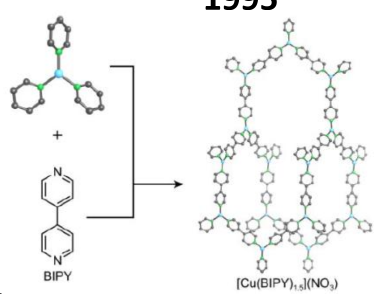
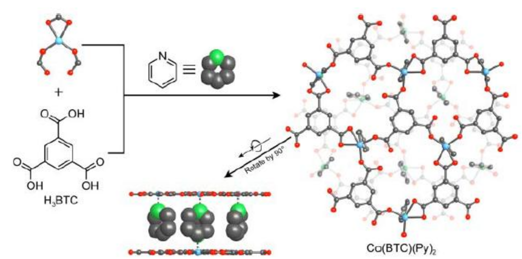


The term metal-organic framework is coined for the first time (Yaghi)



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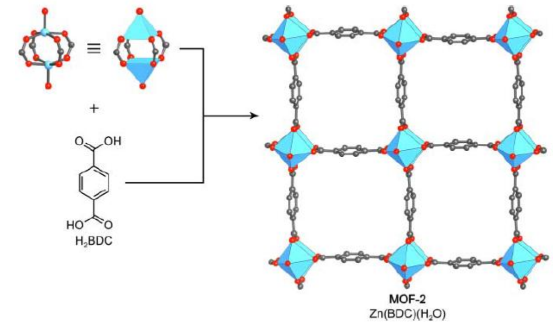

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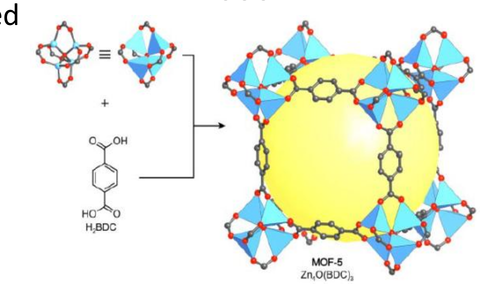

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Coordination Networks

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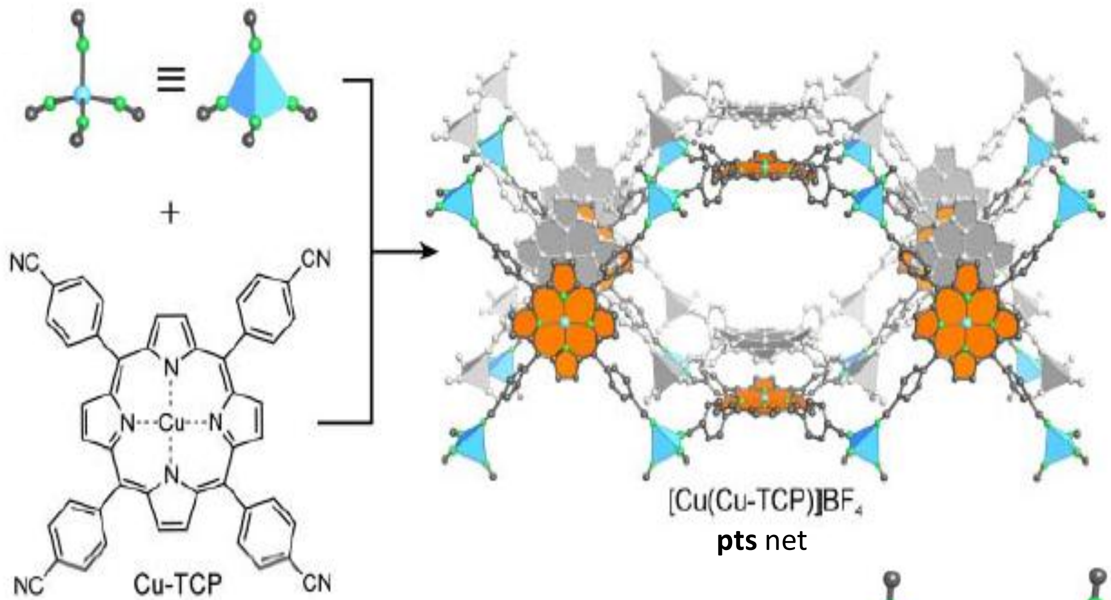
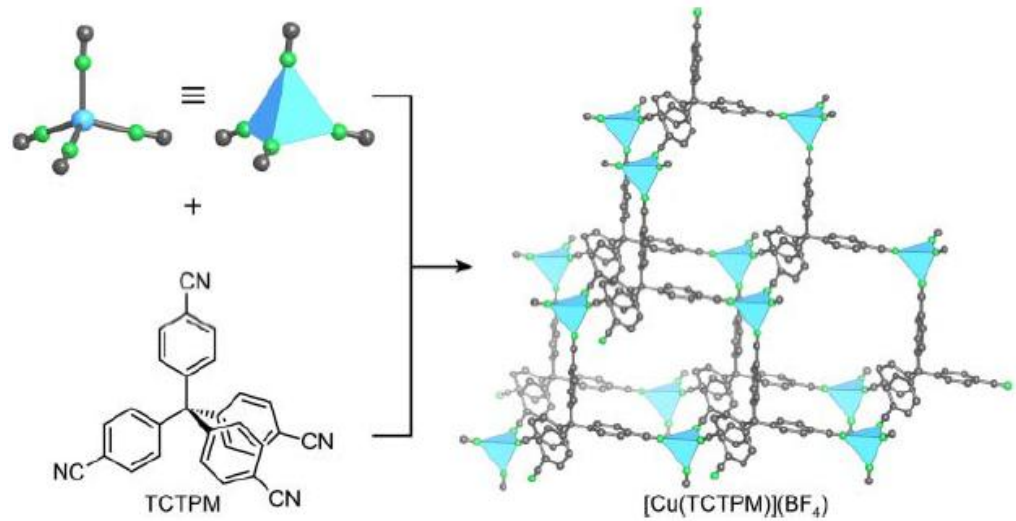


pts net



dia topology

B.F. Hoskins and R. Robson, *Journal of the American Chemical Society,* **1989**, 111 5962–5964.
R.W. Gable, B.F. Hoskins and R. Robson, *Chemical Communications*, **1990**, 10 762–763.
B.F. Abrahams, B.F. Hoskins, D.M. Michail and R. Robson, *Nature,* **1994**, 369 727–729

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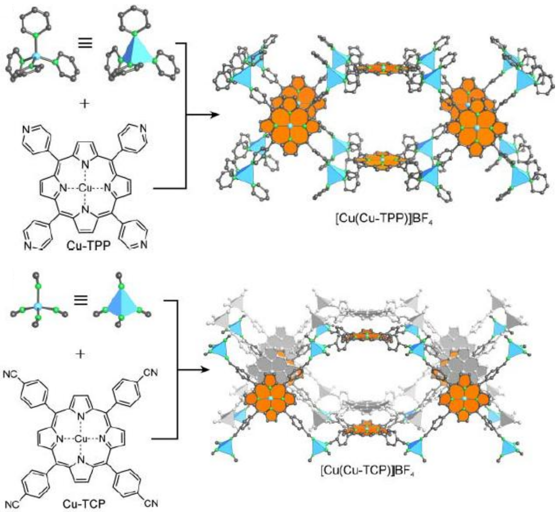

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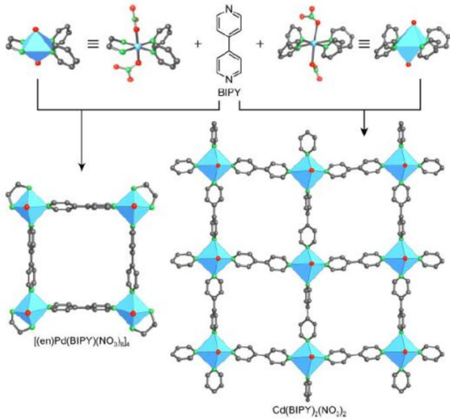

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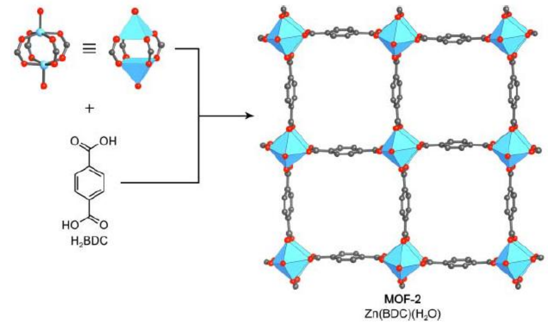

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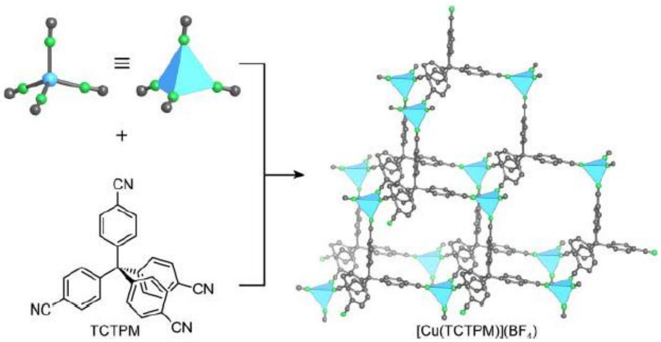

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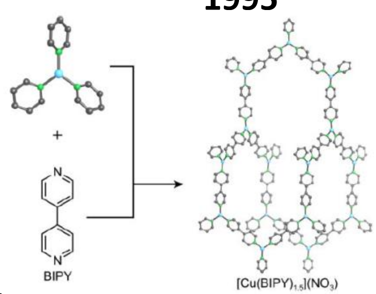

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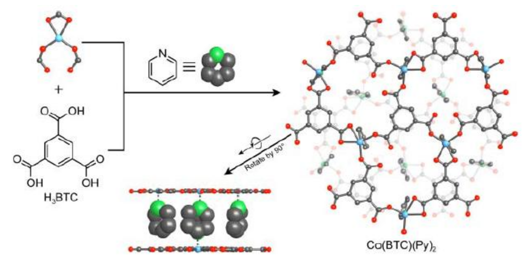

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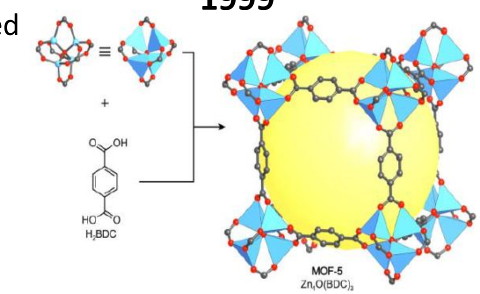

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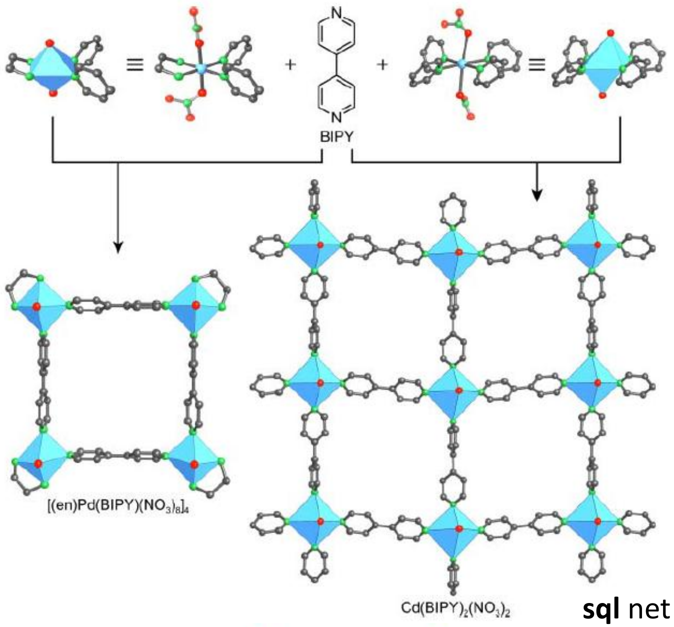
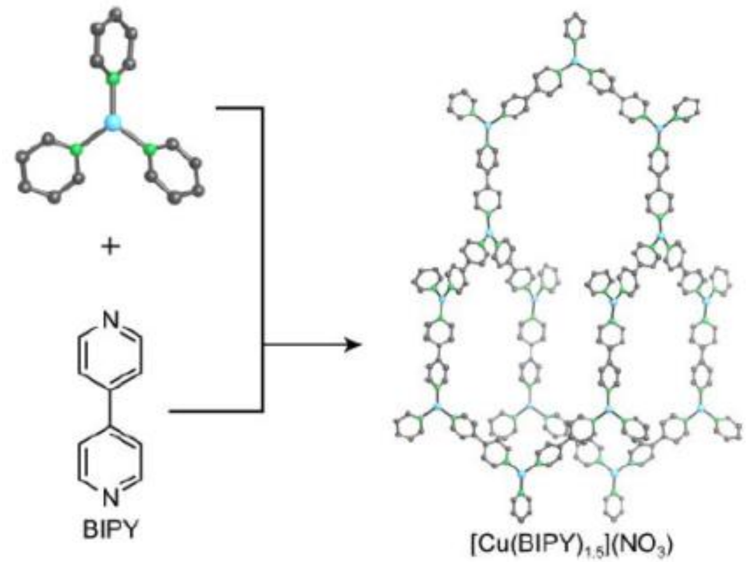


sql net



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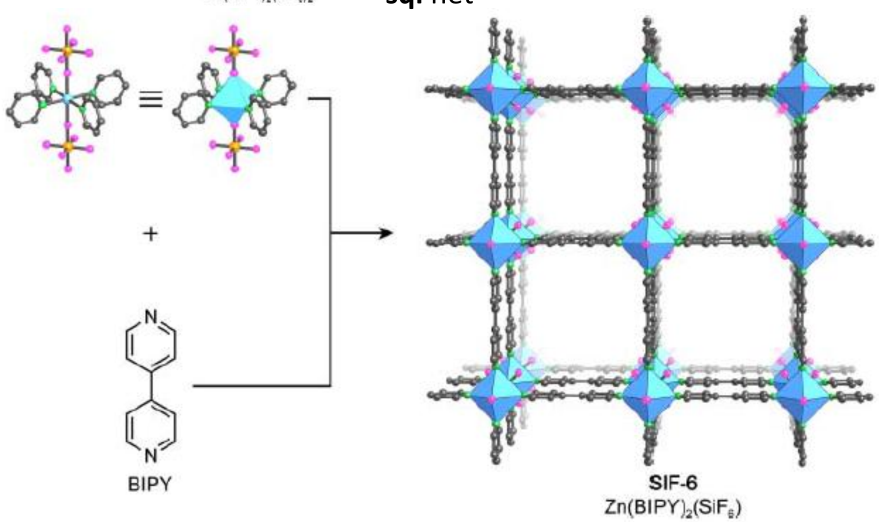


sql net → 3D **pcu** network

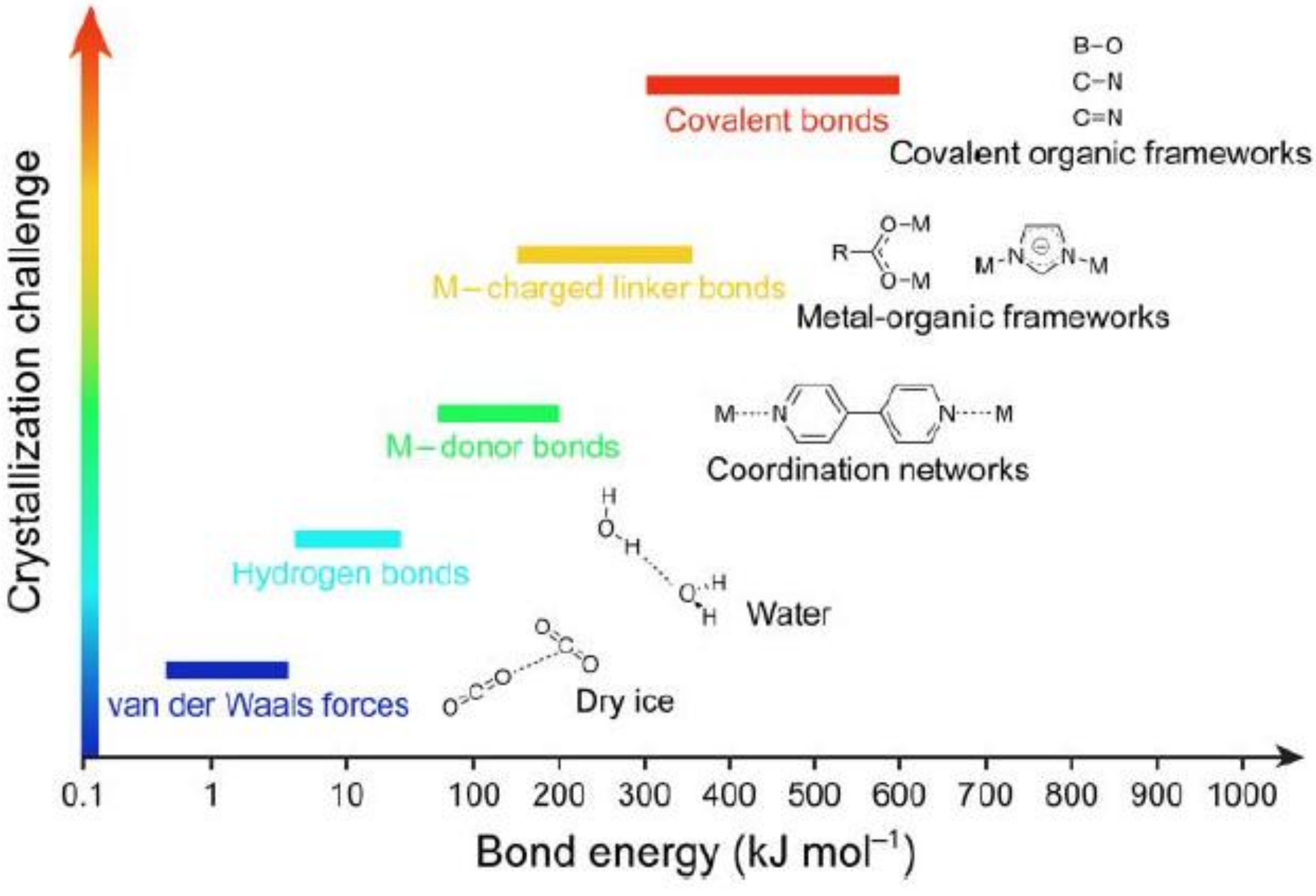
M. Fujita, J. Yazaki and K. Ogura, *Journal of the American Chemical Society,* **1990**,112 5645–5647.
O. Yaghi and H. Li, *Journal of the American Chemical Society,* **1995**, 117 10401–10402.
S. Subramanian and M.J. Zaworotko, **1995**, *Angewandte Chemie, 34 2127–2129.*

Coordination Networks

The aforementioned design principles can be used to construct a wide variety of coordination networks through the judicious choice of metal ions and organic linkers, **BUT**

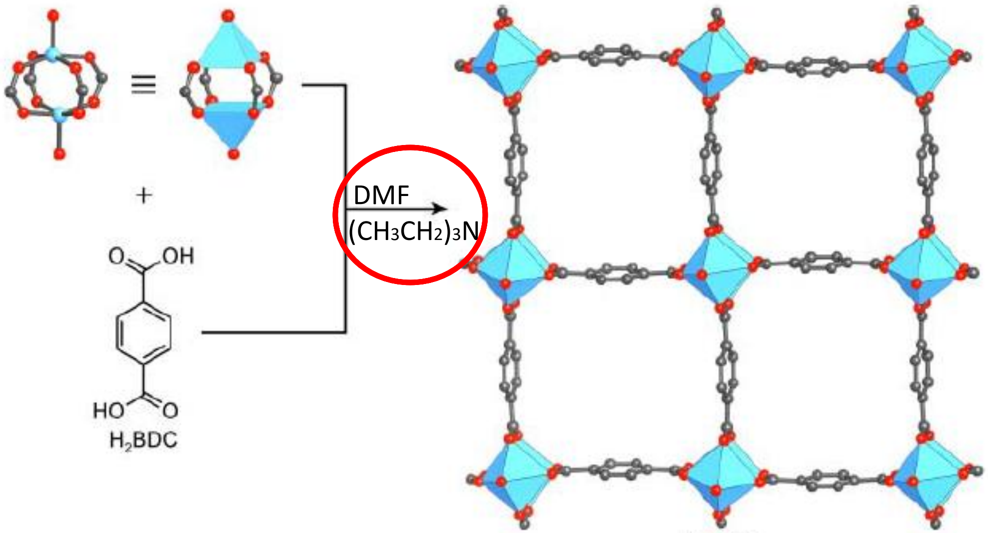
- Collapsed upon removal of solvents or exchange of ions in pores
- Not Designable because they are made of single metal ion vertex
- Chemical instability, because of weak M-N(pyridine, nitrile) –type of links

Crystallization problem



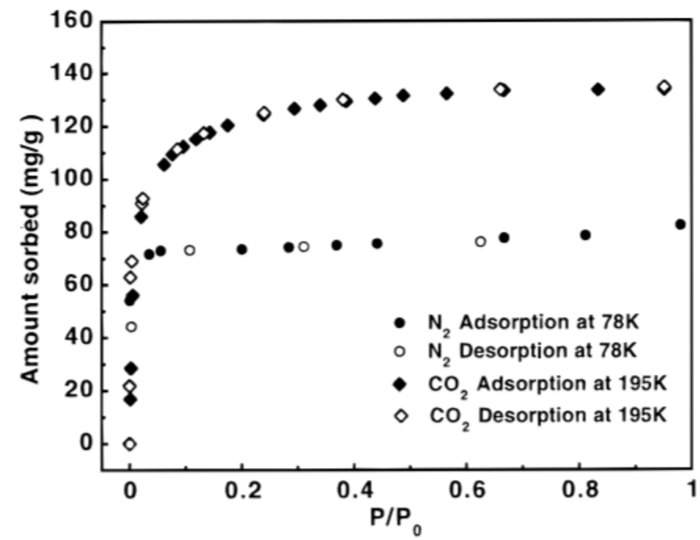
MOF-2

(Introduction of SBUs and charged linkers) for the link of ions)



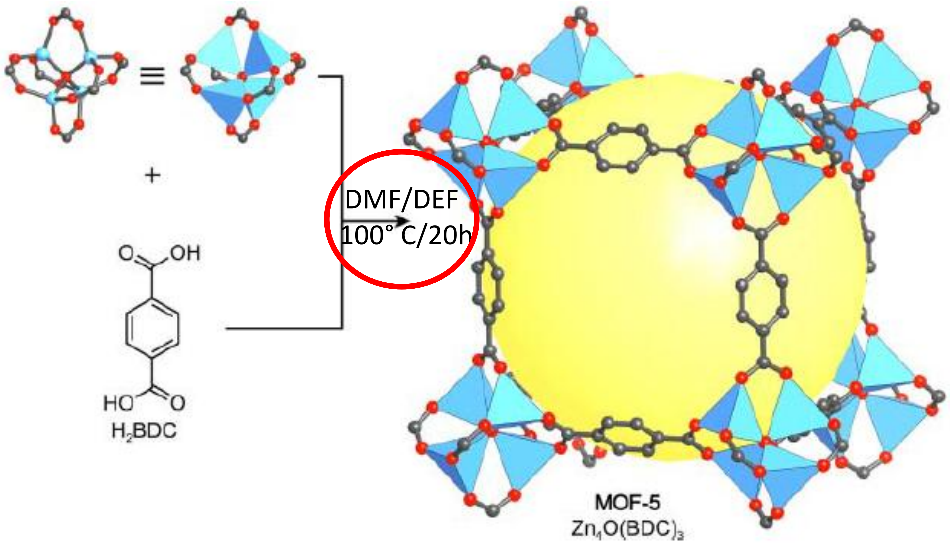
MOF-2
Zn(BDC)(H$_2$O)

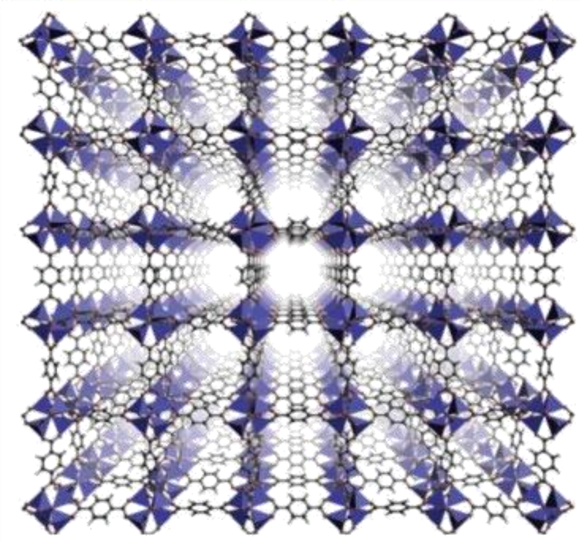
Surface area: 275 m^2/g



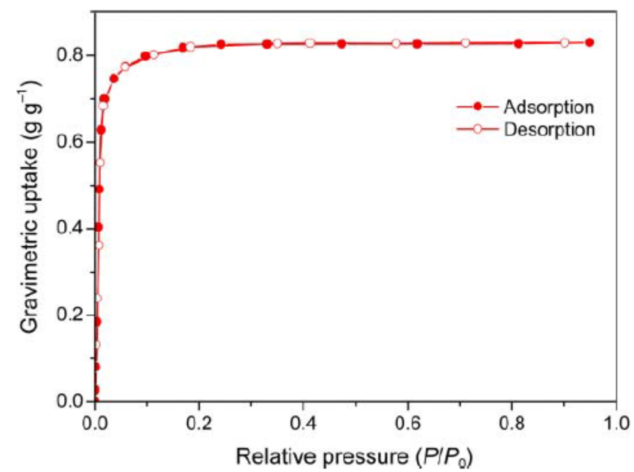
H. Li, M. Eddaoudi, T.L. Groy and O. M. Yaghi, *Journal of the American Chemistry Society,* **1998**, *120 (33): 8571–8572.*

MOF-5





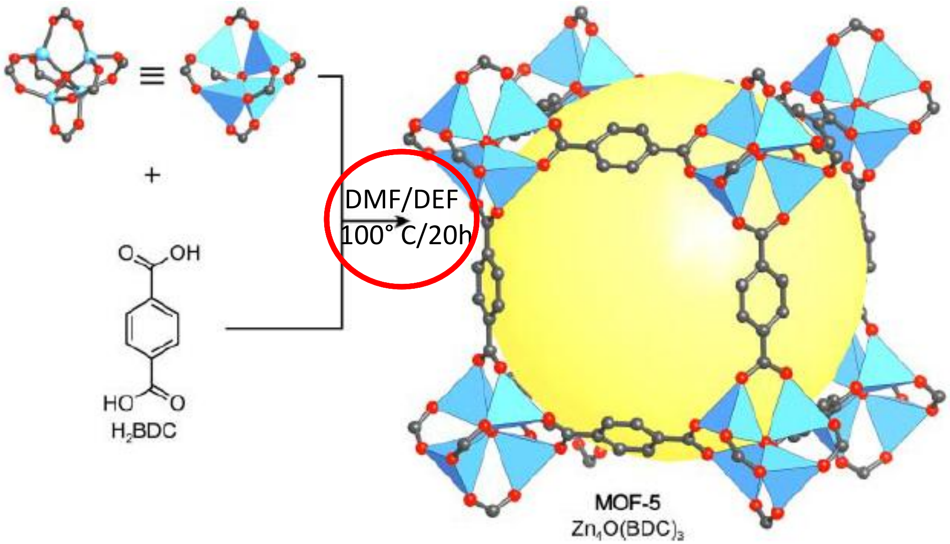
Surface area: 2900 m^2/g

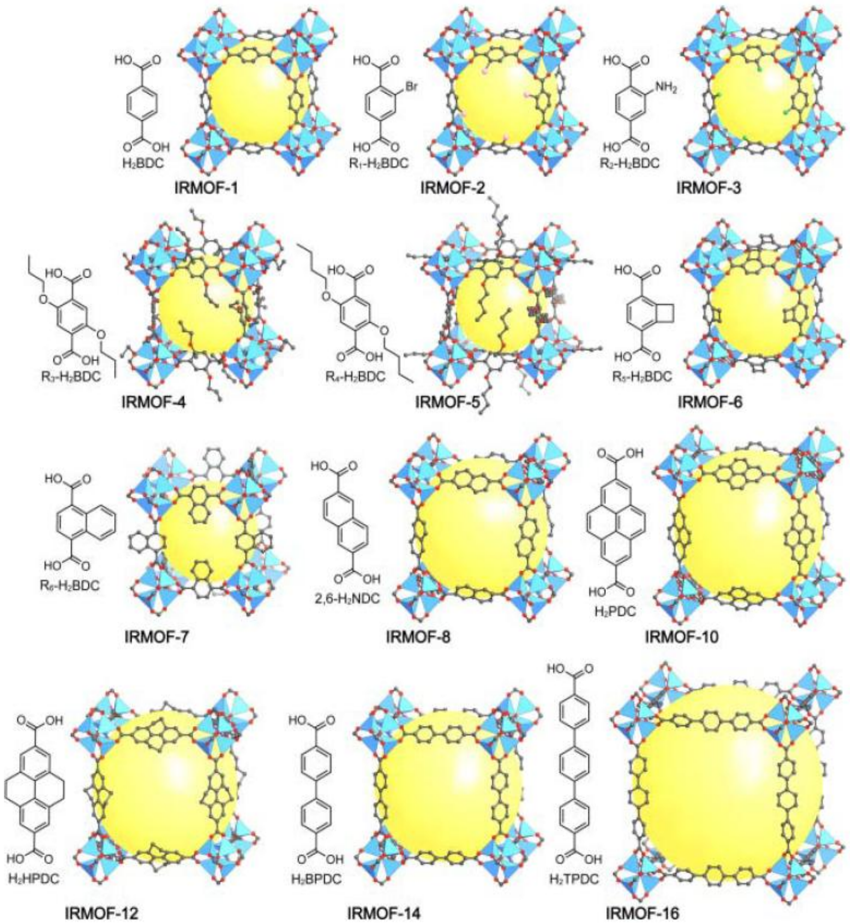


H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature,* **1999**, 402 (6759): 276–279.

MOF-5

Isoreticular principle: elongation(pore opening) or functionalization of the linker without modifying its general shape and connectivity





M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science,* **2002**, 295 (5554): 469–472.

- *"One of the continuing scandals in the physical sciences is that it remains general **impossible to predict the structure** of even the simplest crystalline solids from a knowledge of their chemical composition"*

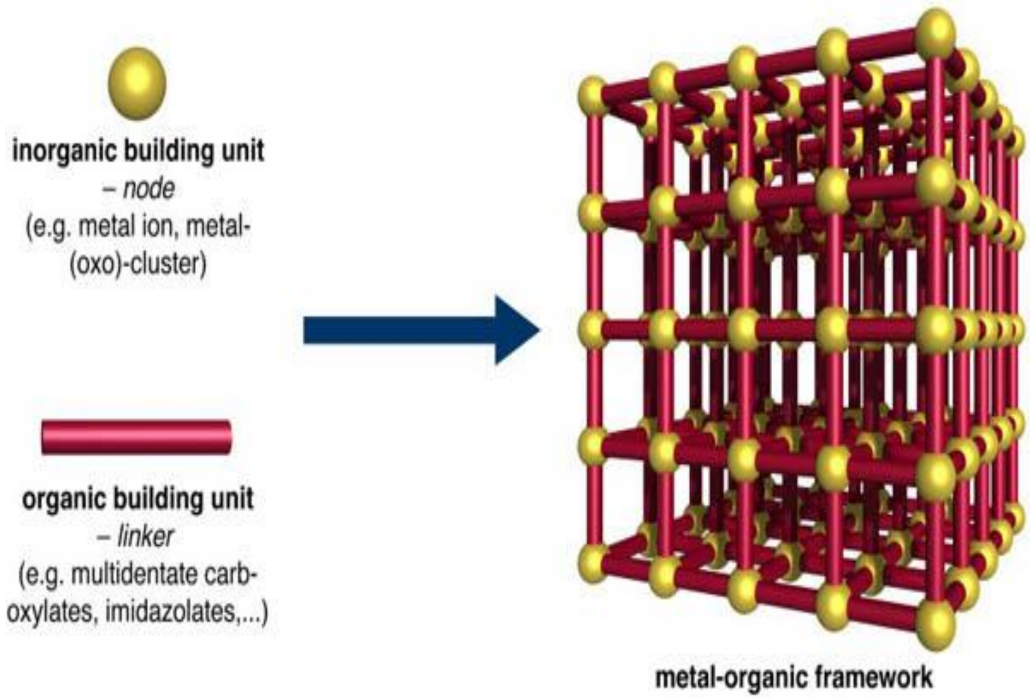
John Maddox, *Nature*, **1988**, 335, 201.

- *"Organic chemists are masterful at exercising control in zero dimension. One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders…But **in two or three dimensions, it is a synthetic wasteland**."*

R.Hoffmann, *Scientific American*, **1993**, 65-73.

Reticular chemistry: is the study of linking **molecular building blocks** by **strong** to make **crystalline** extended structures.

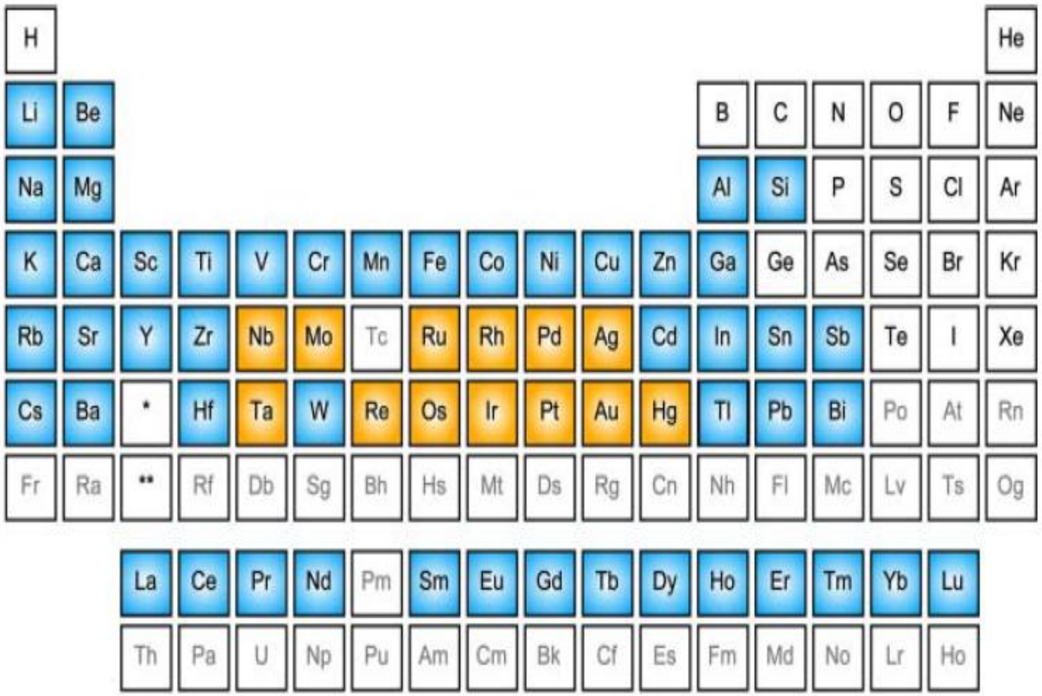
Design

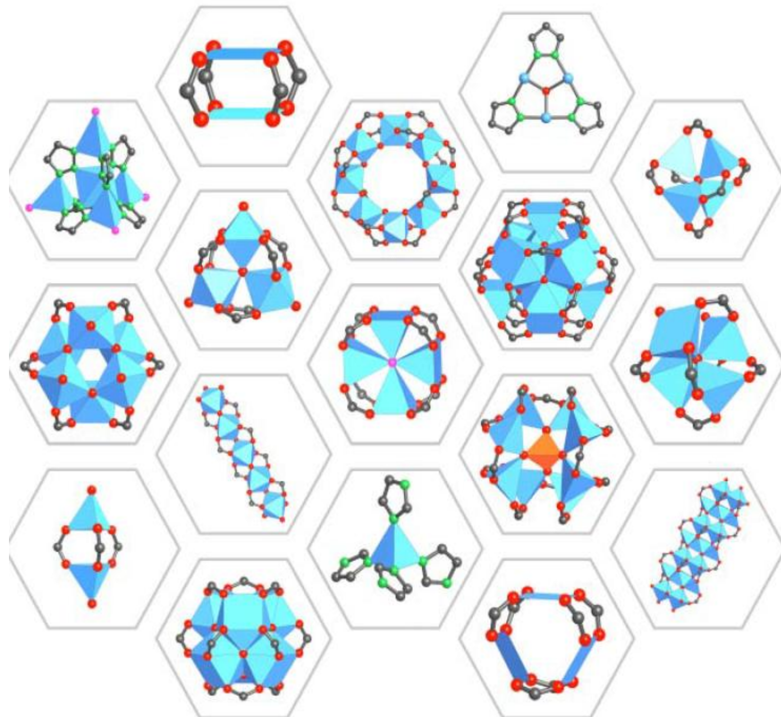


inorganic building unit
– *node*
(e.g. metal ion, metal-
(oxo)-cluster)
organic building unit
– *linker*
(e.g. multidentate carb-
oxylates, imidazolates,...)
metal-organic framework

Design

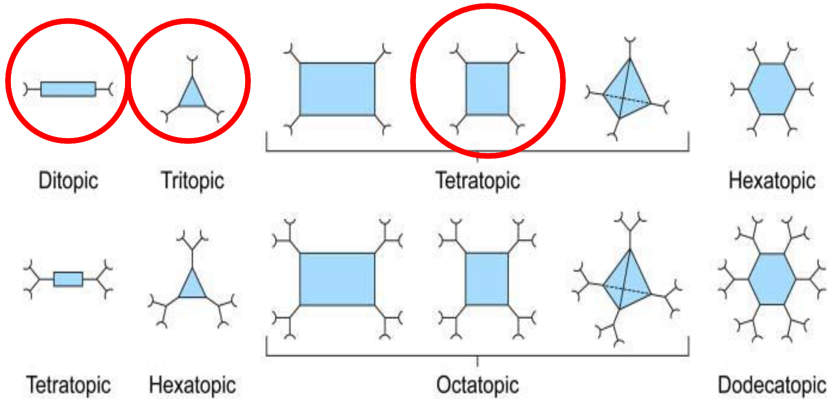
(Secondary Building Units, SBUs)

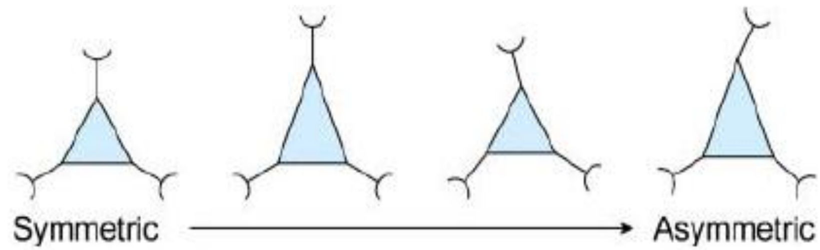


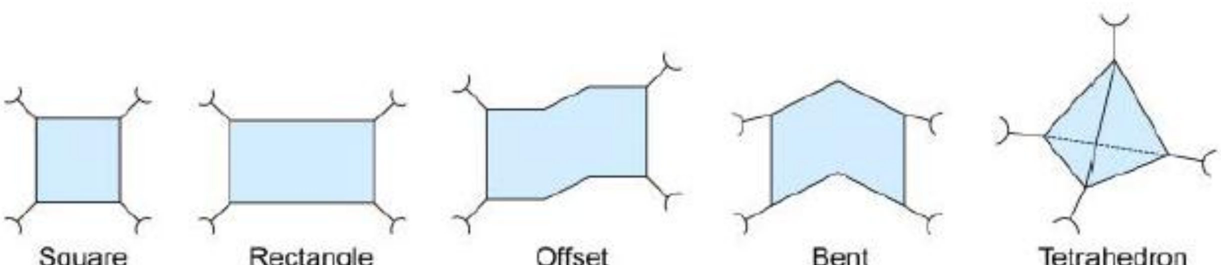


Design

(Organic linker)

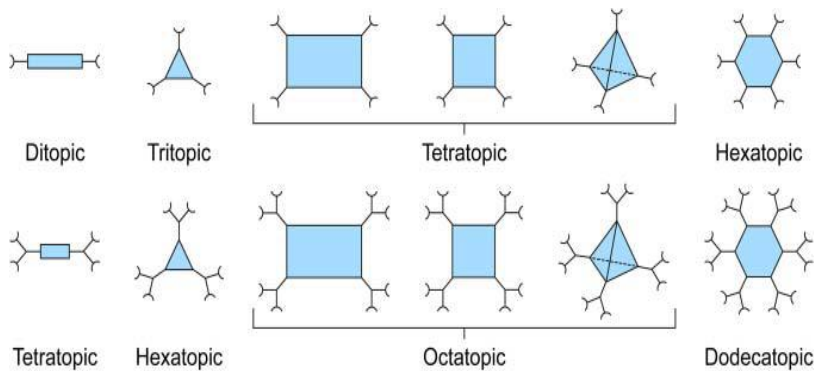


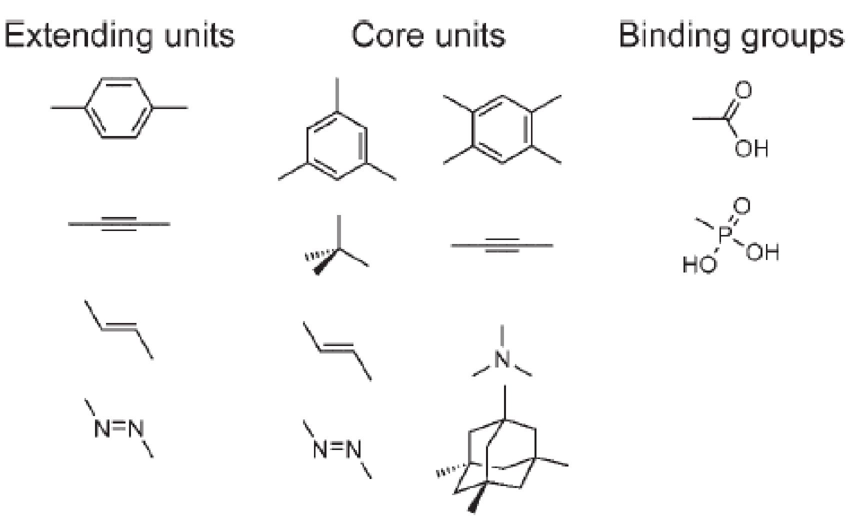


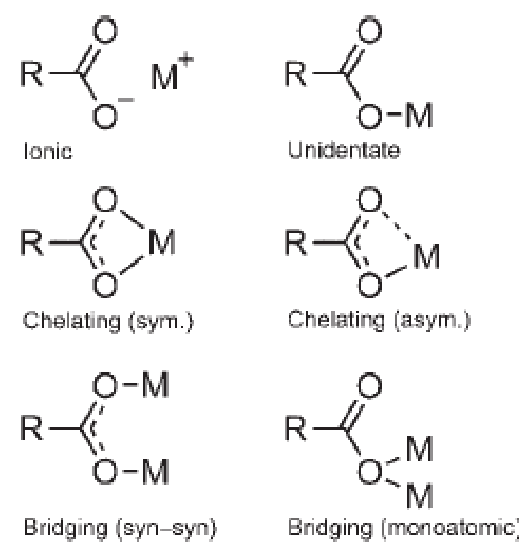


Design

(Organic linker)

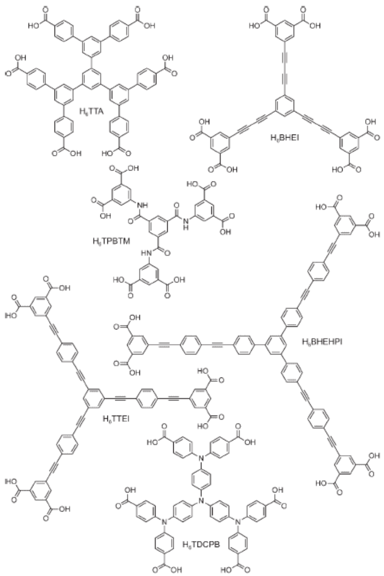


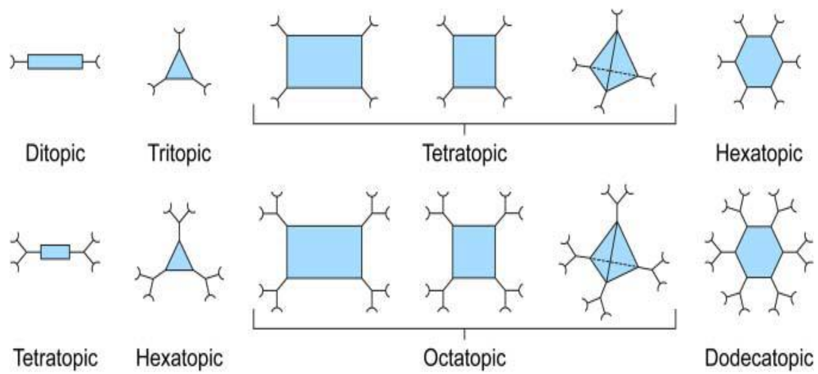


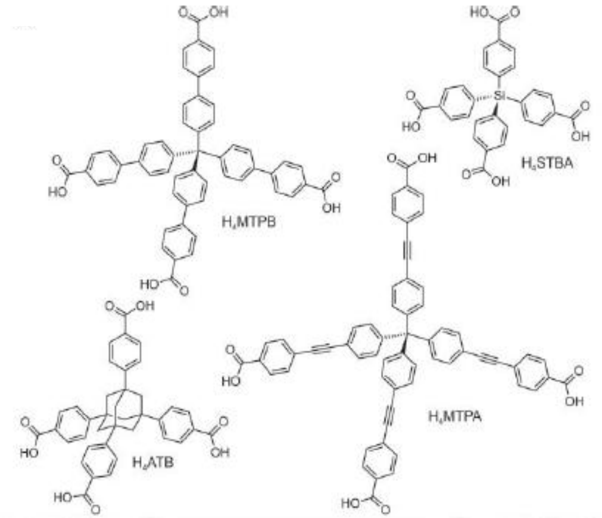


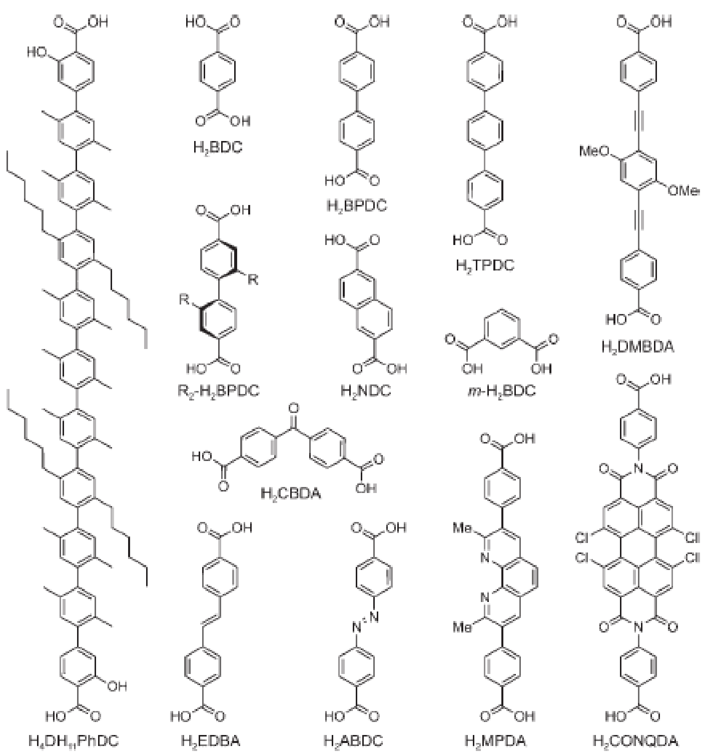
Design

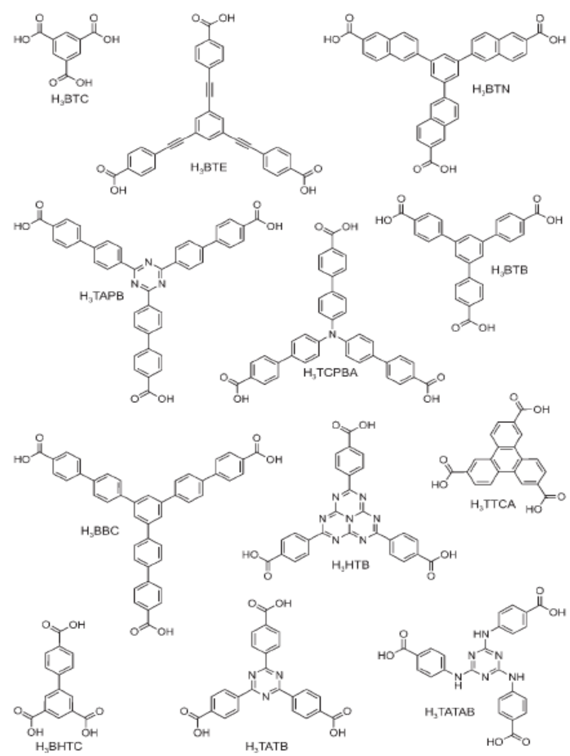
(Organic linker)

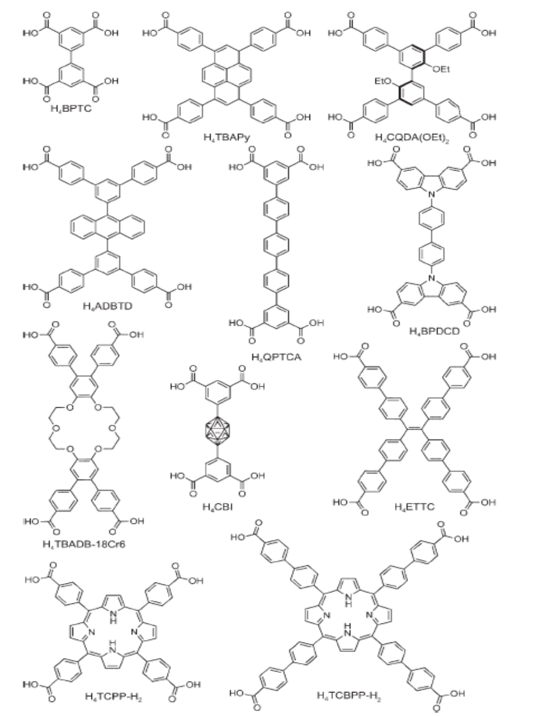






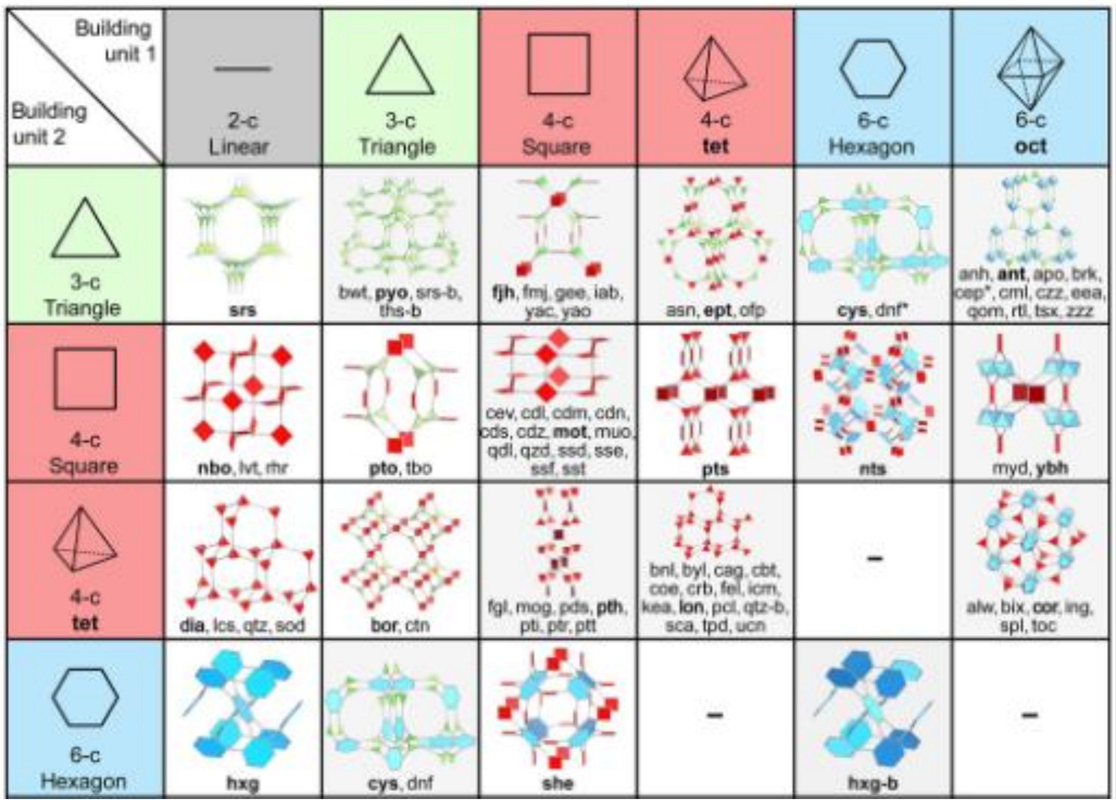






Design

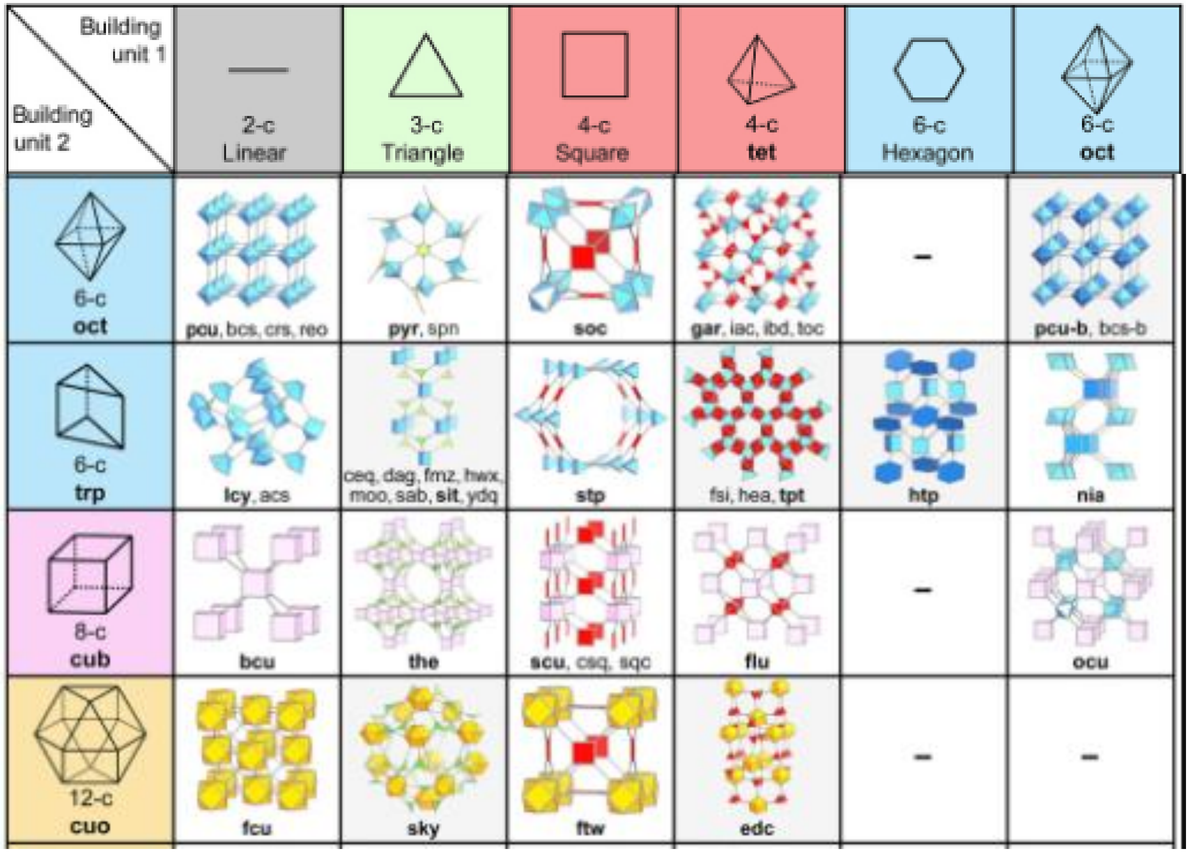
(Application of SBU approach)



M. J. Kalmutzki, N. Hanikel and O. M. Yaghi, *Science Advances,* **2018**, 4, 10.

Design

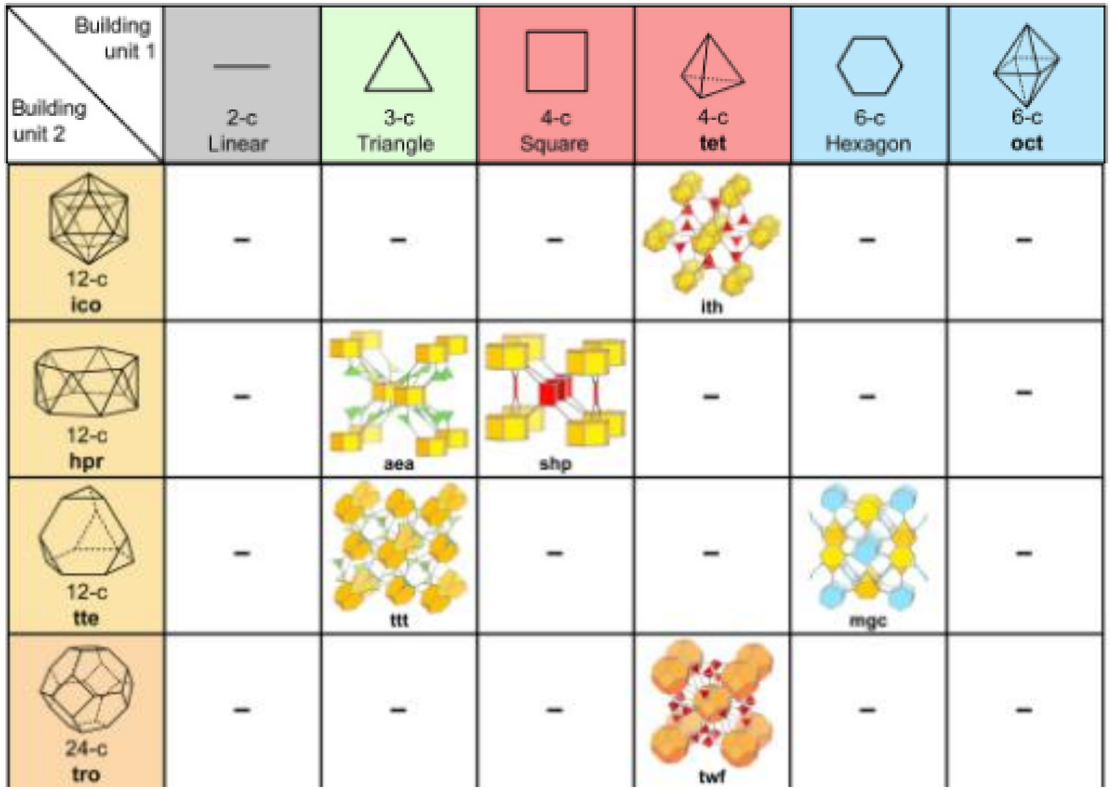
(Application of SBU approach)



M. J. Kalmutzki, N. Hanikel and O. M. Yaghi, *Science Advances,* **2018**, 4, 10.

Design

(Application of SBU approach)

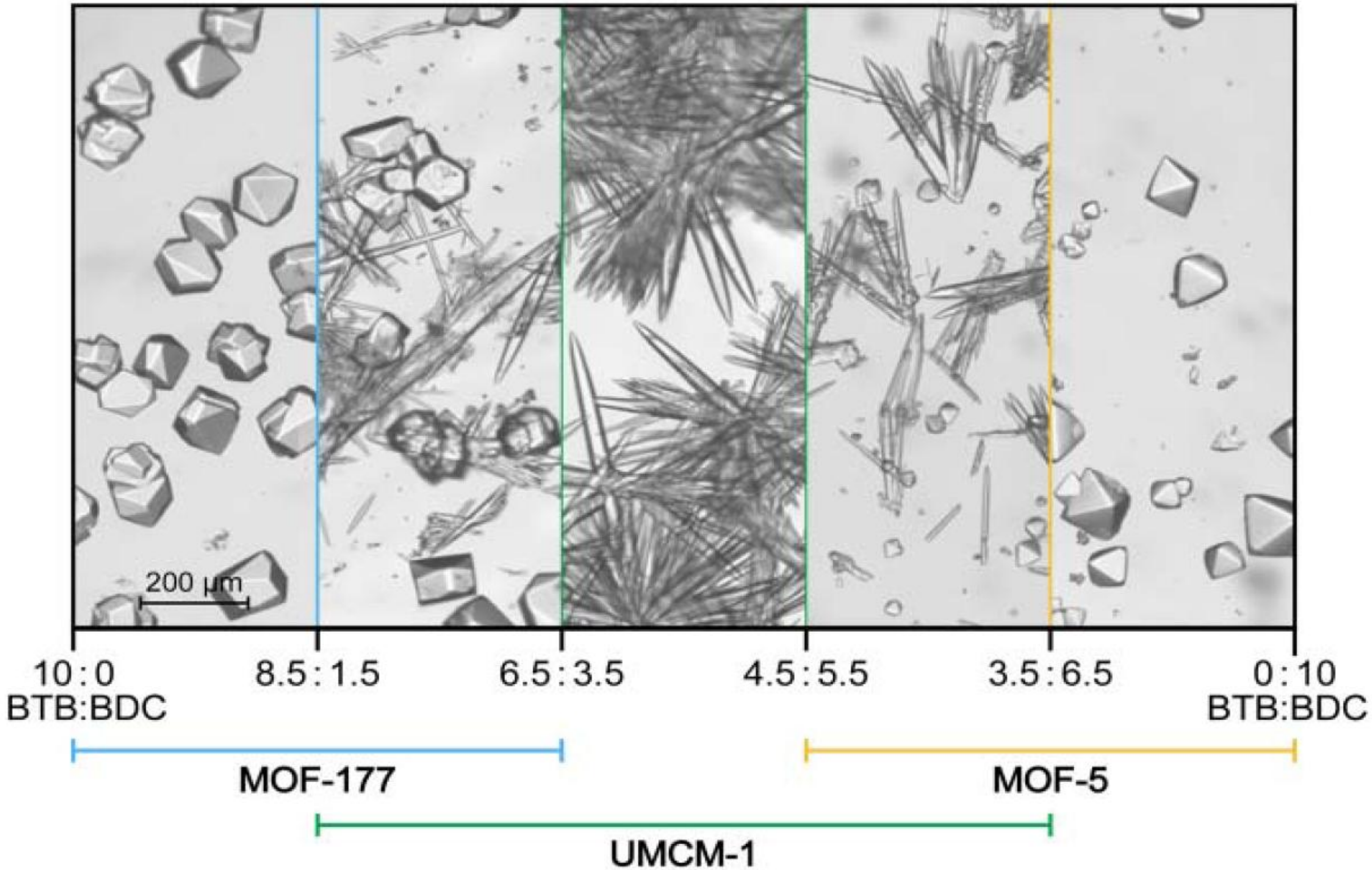


M. J. Kalmutzki, N. Hanikel and O. M. Yaghi, *Science Advances,* **2018**, 4, 10.

Design

(Complexity and Heterogeneity)

Complexity
(i)multiple different linkers
(ii)multiple different SBUs
(iii)multiple different SBUs and linkers



K. Koh, A.G. Wong-Foy and A.J. Matzger, *Angewandte Chemie,* **2008**, 47 (4): 677–680.

Design

(Complexity and Heterogeneity)

Complexity

(i)multiple different linkers

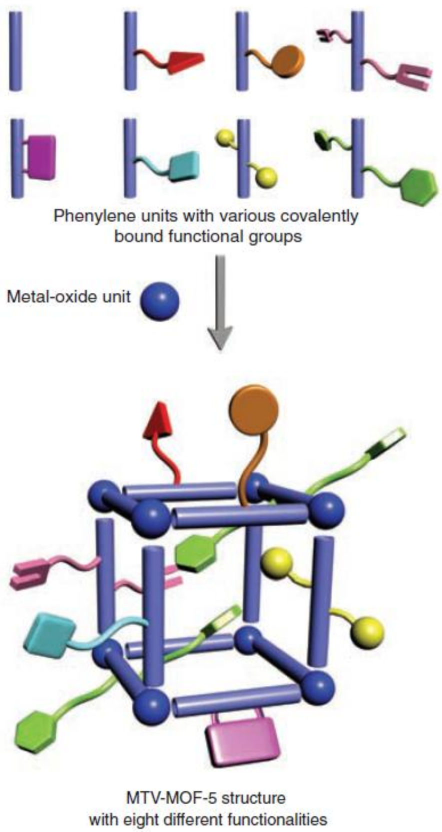
(ii)multiple different SBUs

(iii)multiple different SBUs and linkers

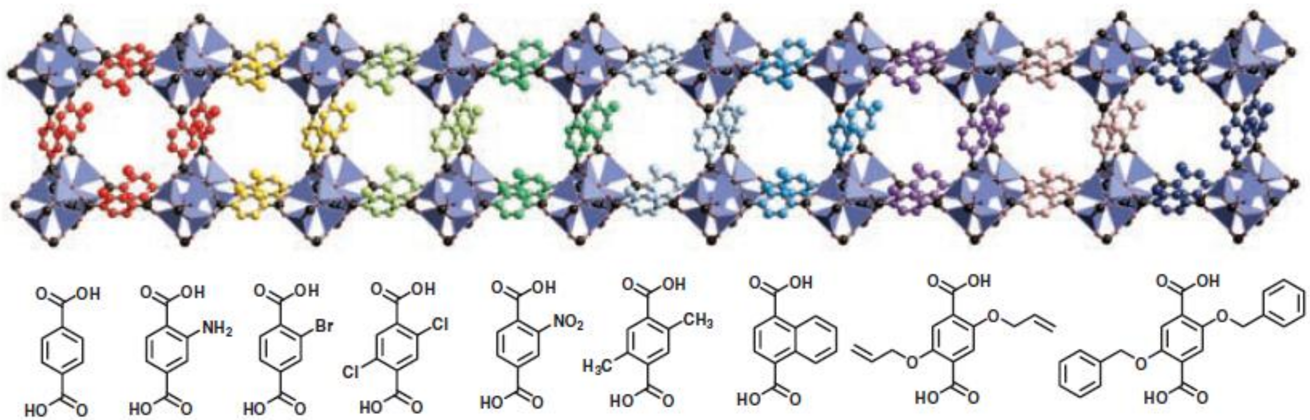
Heterogeneity

(i) multiple interchangeable linkers that are identical in terms of their binding groups and metrics but different with respect to their chemical composition

(ii) multiple metal ions that form the same SBU



MTV-MOF-5



H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science*, **2010**, *327(5967), 846–850.*

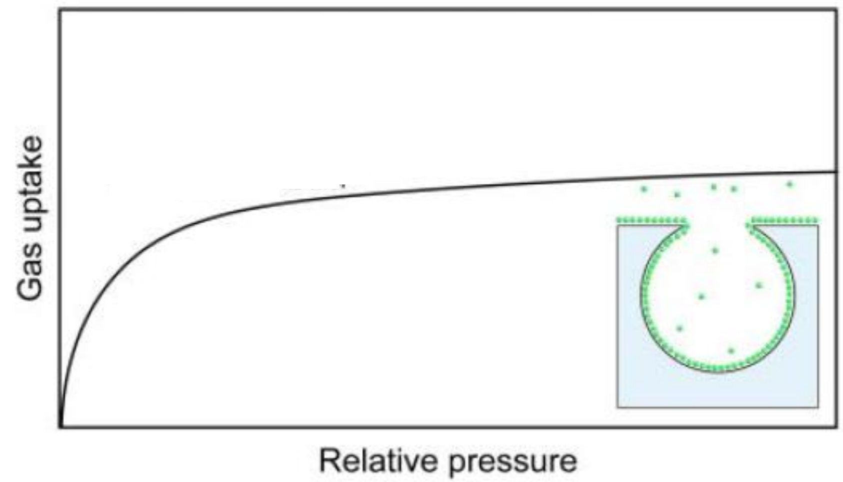
Design

(Fine-tuning of the sorption properties)

Parameters defining porosity

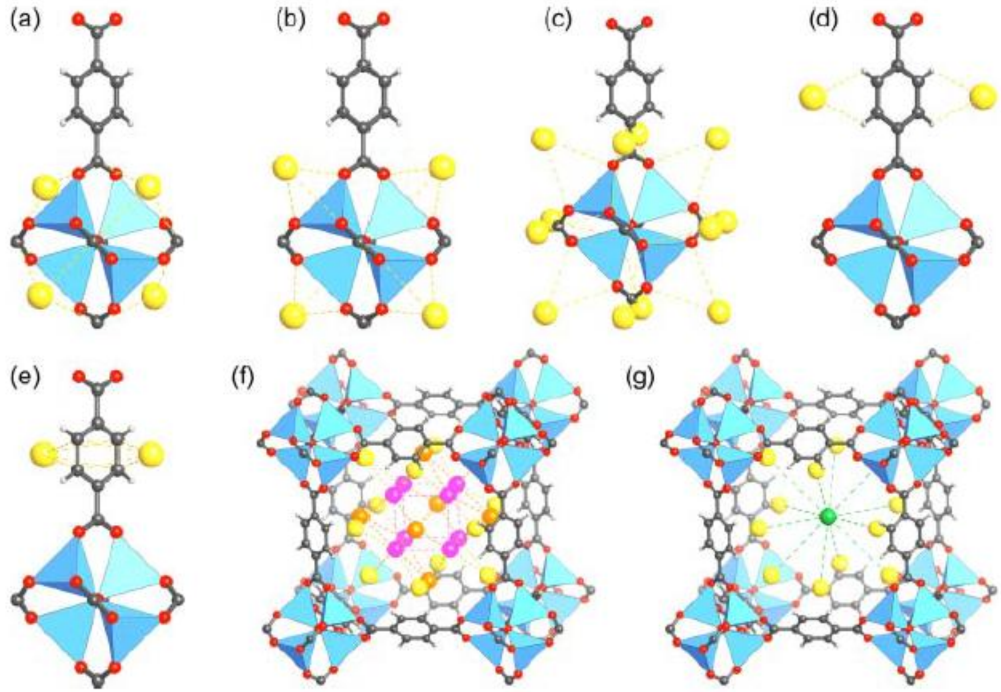
Specific surface area ($m^2\ g^{-1}$) = $\frac{\text{Total surface area } (m^2)}{\text{Mass of the porous solid (g)}}$

Pore size and its distribution



Design

(Ultra-high Surface Area)

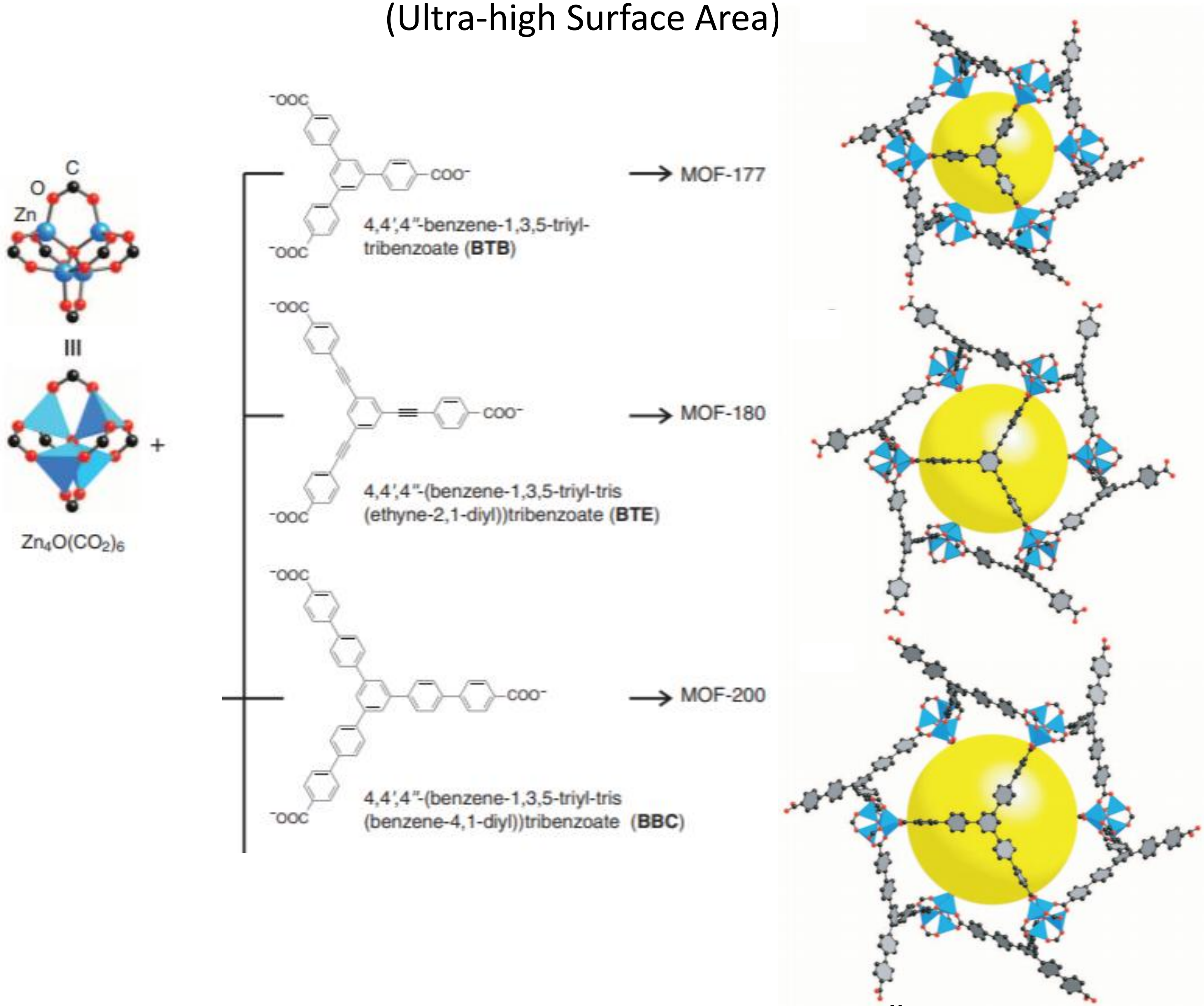


J. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science,* **2005**, 309 1350–1354.

Design

(Ultra-high Surface Area)

BET(m^2/g)



4530

4460

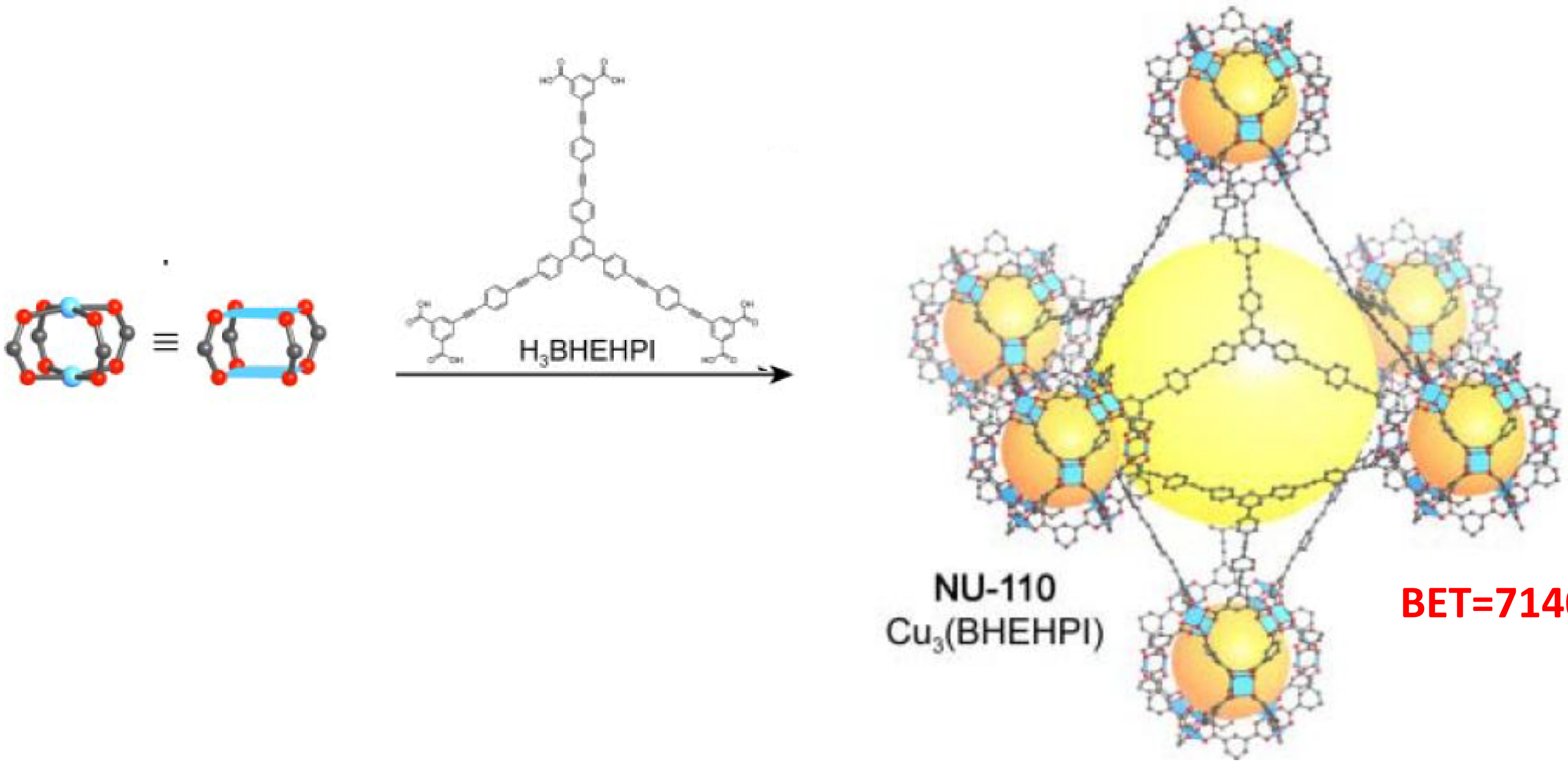
6240

H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. Beom Choi, E. Choi, A. Ö. Yazaydin, R.Q. Snurr, M. O'Keeffe, J. Kim, O. M. Yaghi, *Science,* **2010**, 329(5990), 424–428.

Design

(Ultra-high Surface Area)

Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit?

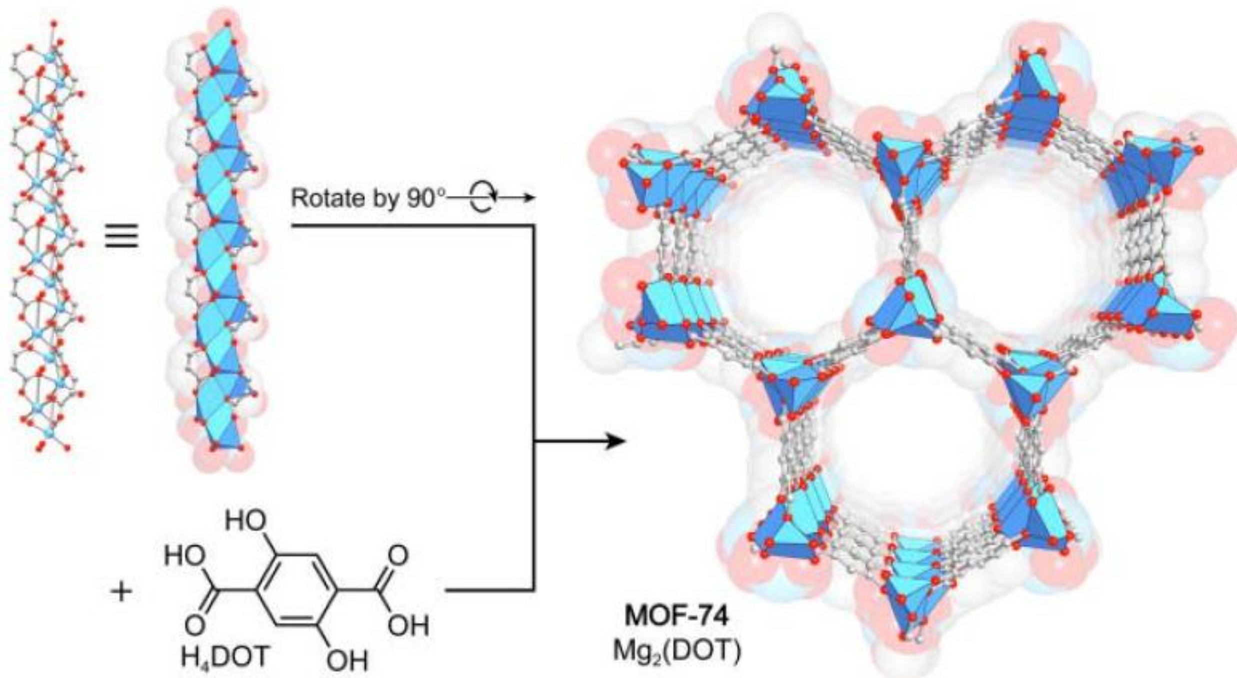


BET=7140m^2/g

O. K. Farha, I. Eryazici, N. Cheon Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R.Q. Snurr, S. T. Nguyen, A. Ö. Yazaydın and J. T. Hupp , *JACS,* **2012**, 134, 36, 15016-15021.

Design

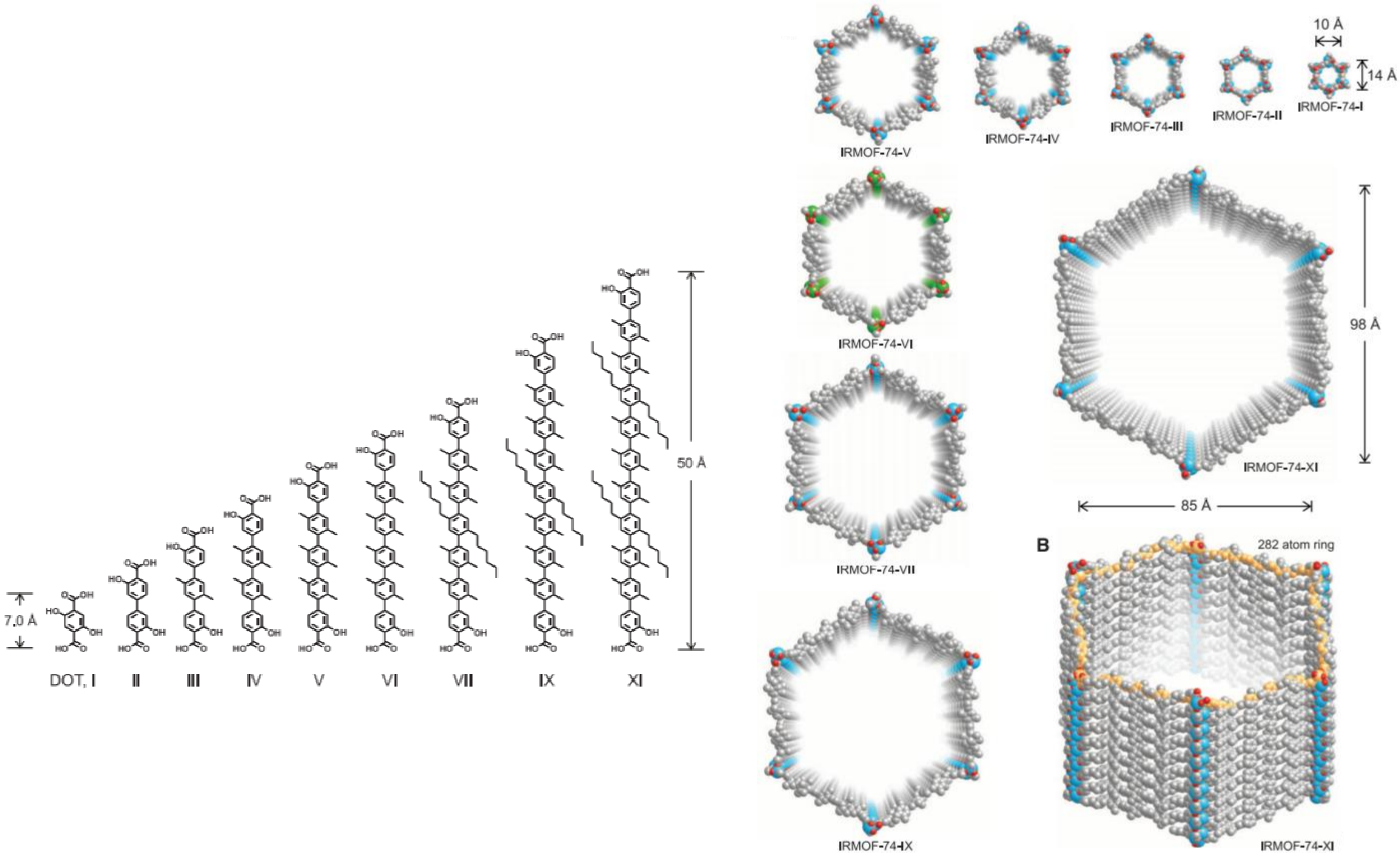
(Pore opening)



N.l L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, *JACS,* **2005**, 127, 5, 1504-1518.

Design

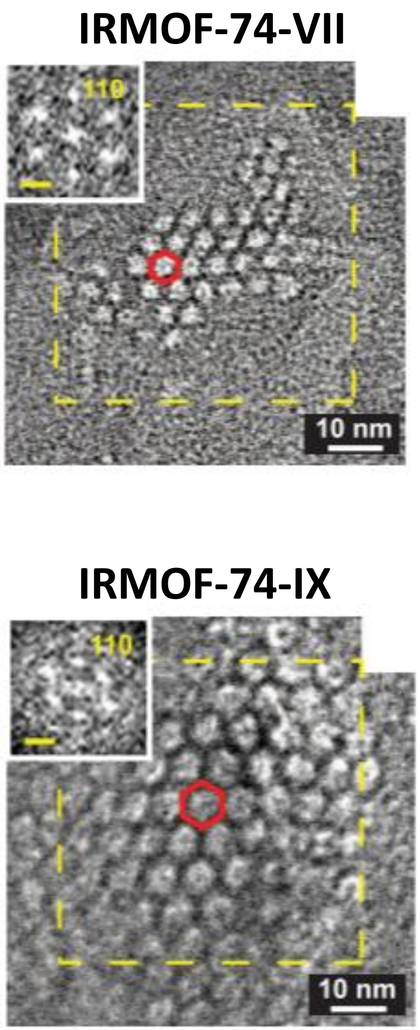
(Pore opening)

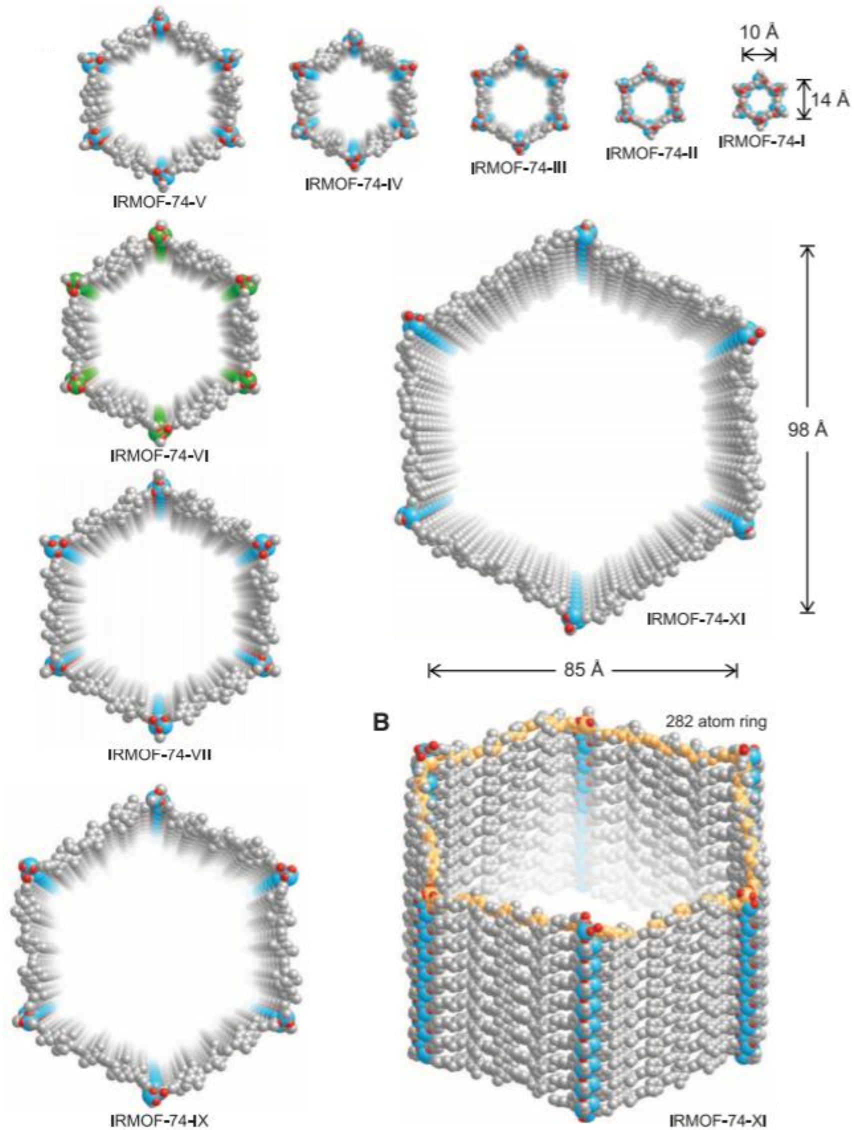


H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z.Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science,* **2012**, 336(6084.

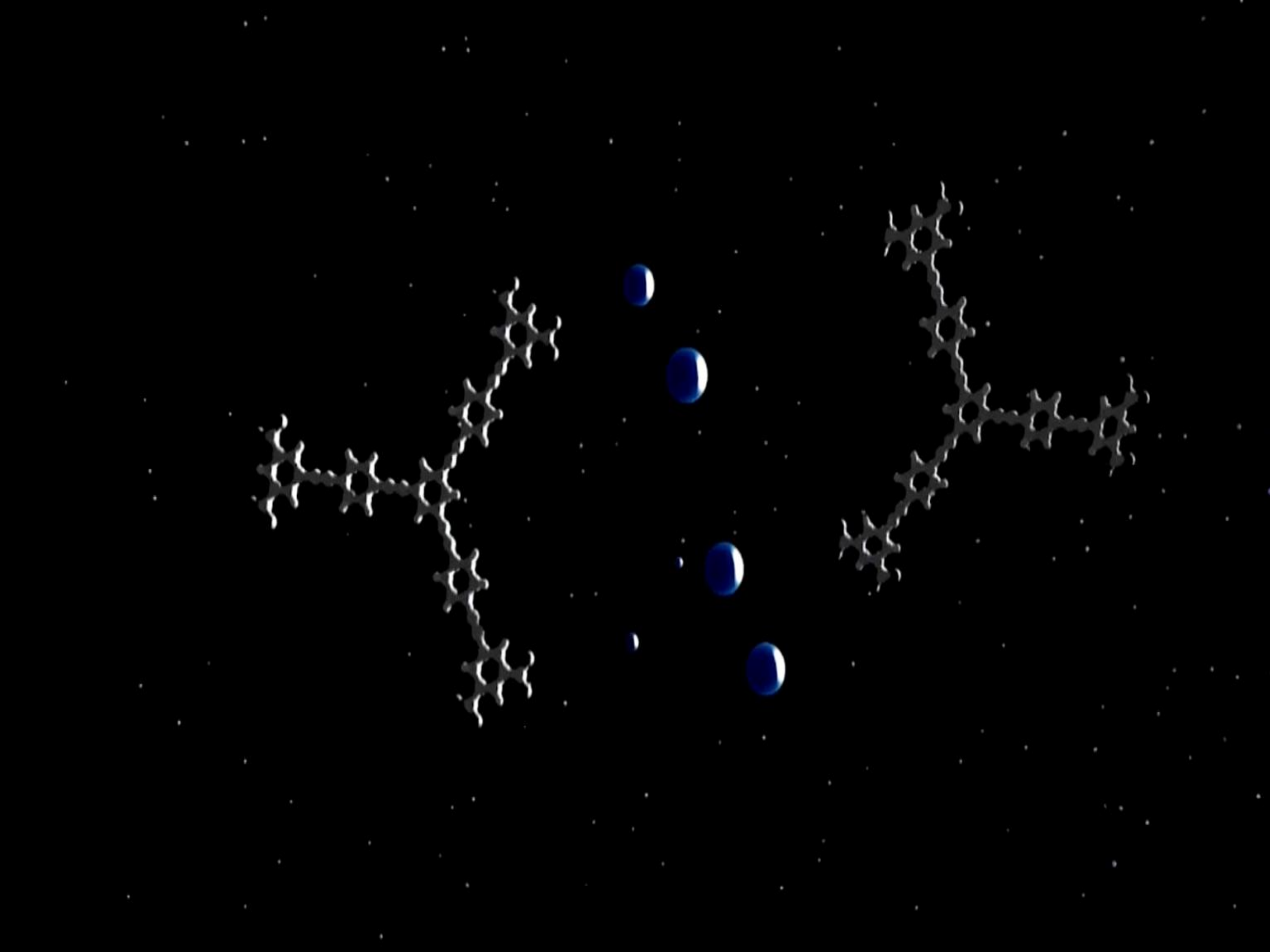
Design

(Pore opening)

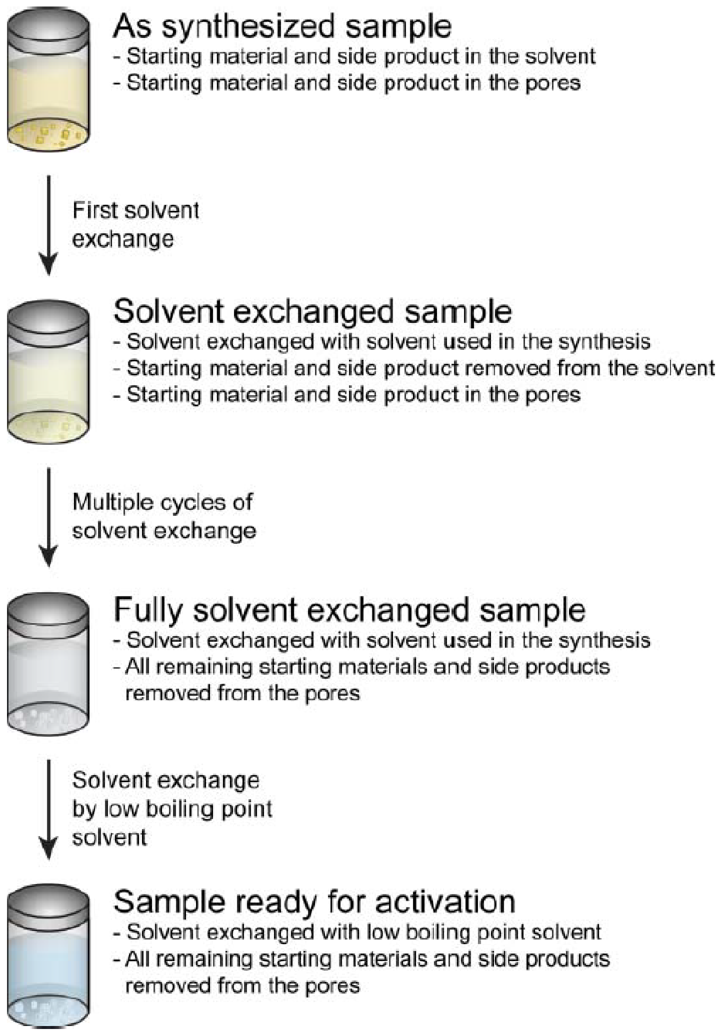




H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z.Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science,* **2012**, 336(6084.



Synthesis-Activation of MOFs



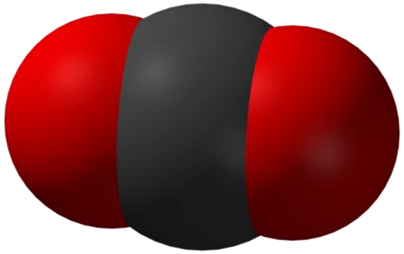
J. E. Mondloch, O. Karagiaridi, O. K. Farha and J. T. Hupp, *CrystEngComm,* **2013**, 15, 9258
A.P. Nelson, O.K. Farha, K.L. Mulfort and J.T. Hupp, *JACS,* **2008**, 131, 458-460.

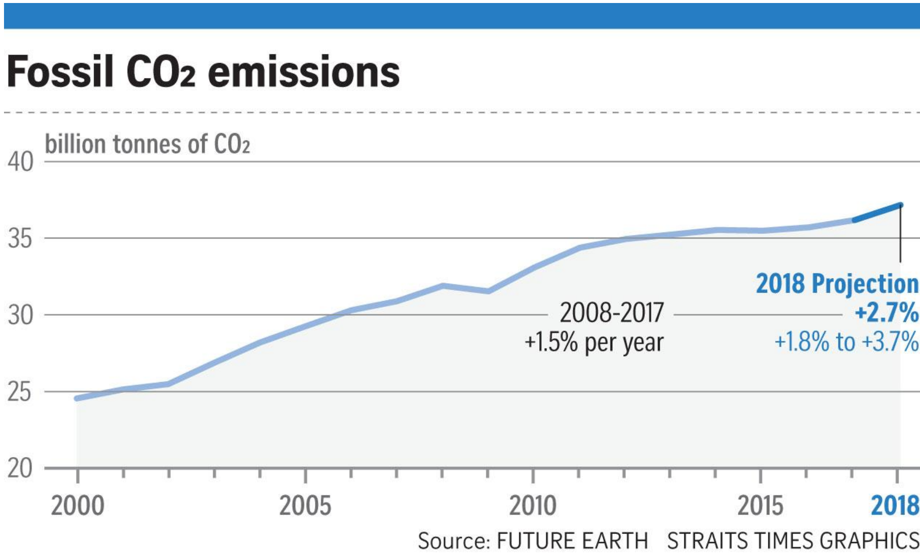
Synthesis-Activation of MOFs

(Modulated synthesis)

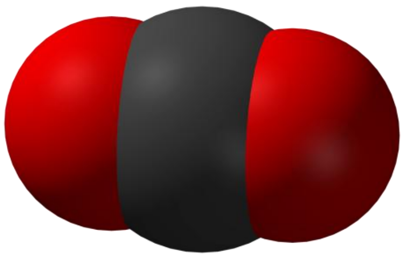
A.J. Howarth, Y. Liu, P. Li, Z. Li, T.C. Wang, J. T. Hupp and O. K. Farha, *Nature Review Materials,* **2016,** 1, 15018.

Applications of MOFs

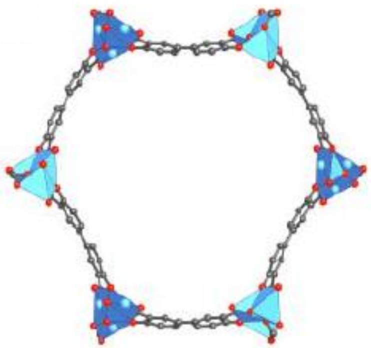


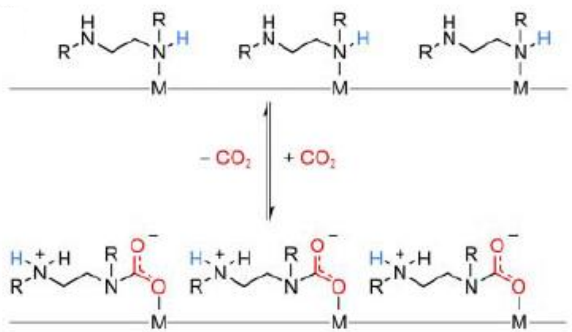


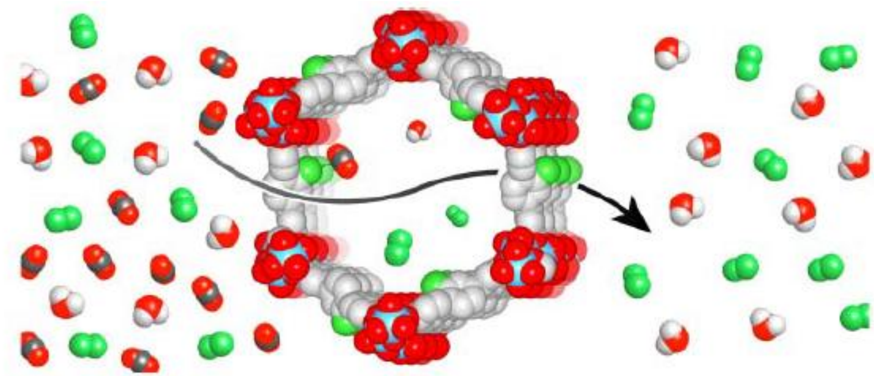
Applications of MOFs

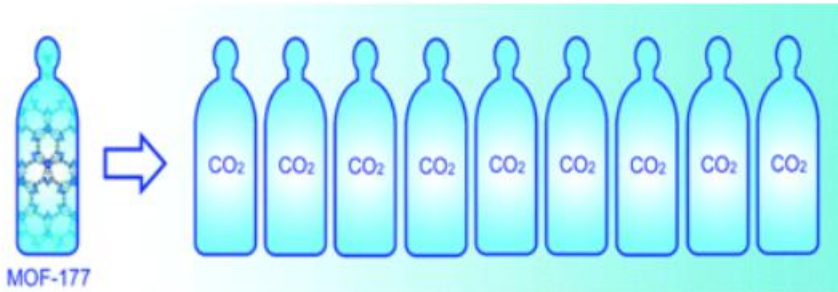


CO_2 capture/separation
- Open metal sites
- Amine groups



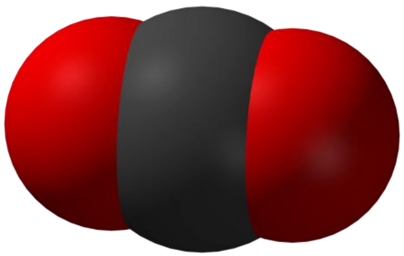


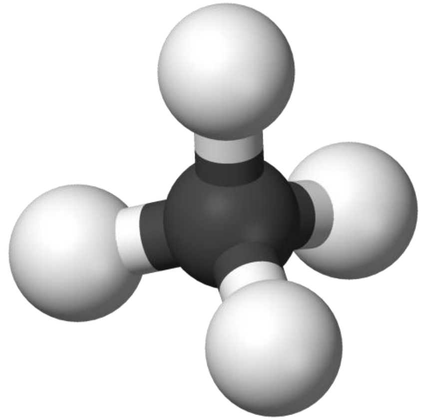


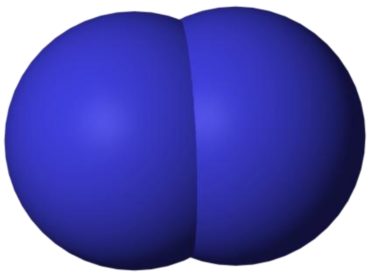


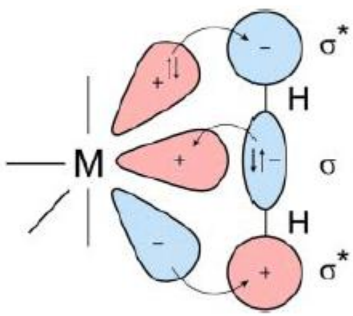
P. J. Milner, R. L. Siegelman, A. C. Forse, M. I. Gonzalez, T. Runčevski, J. D. Martell, J. A. Reimer and J. R. Long, *JACS,* **2017,** 139, 38, 13541-13553.

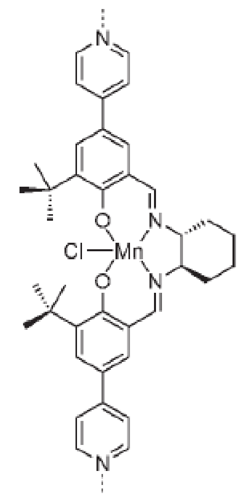
Applications of MOFs

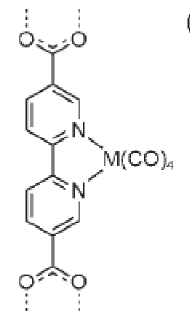






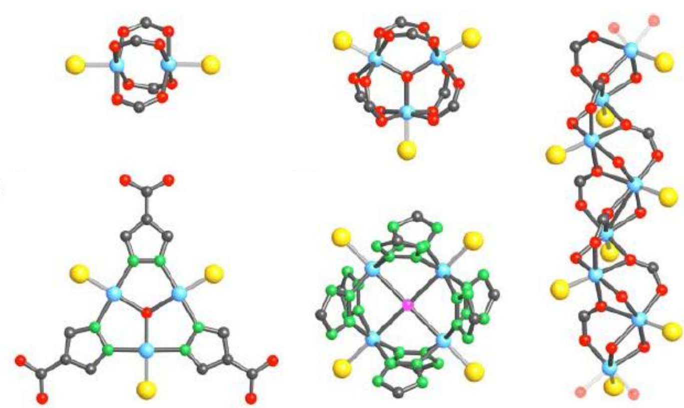




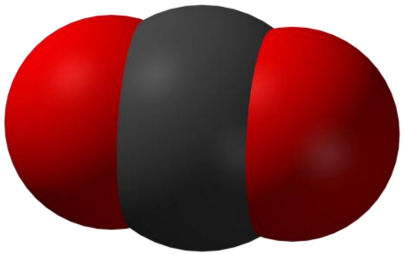


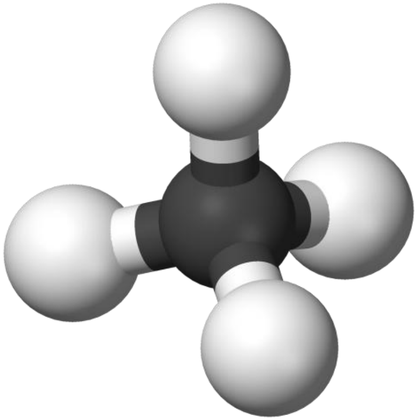
H_2 and CH_4 storage

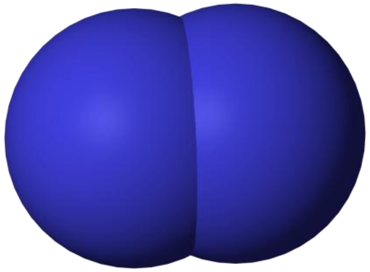
Open metal sites



Applications of MOFs

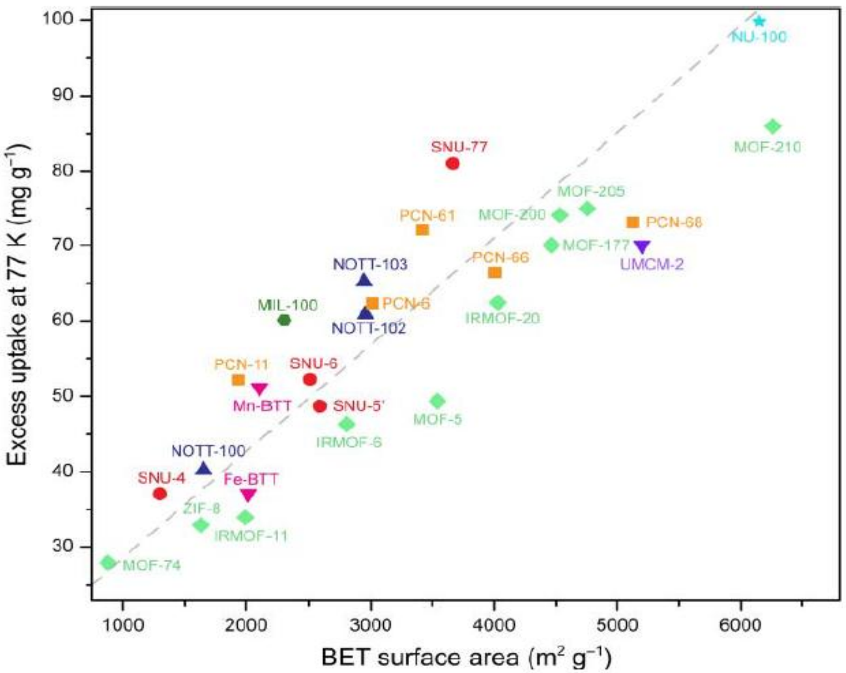




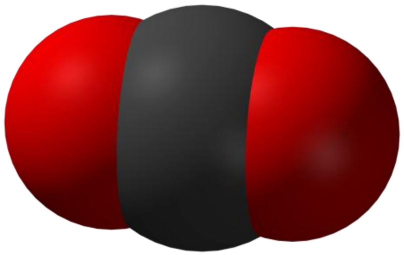


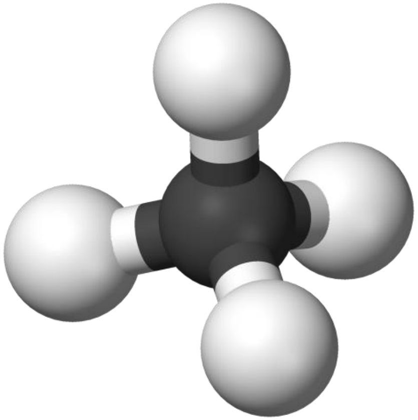
H_2 and CH_4 storage

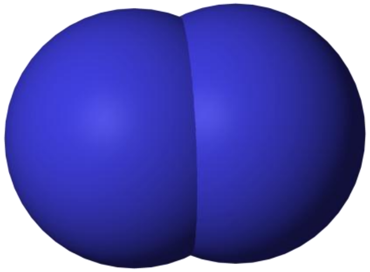
- Open metal sites
- High surface areas

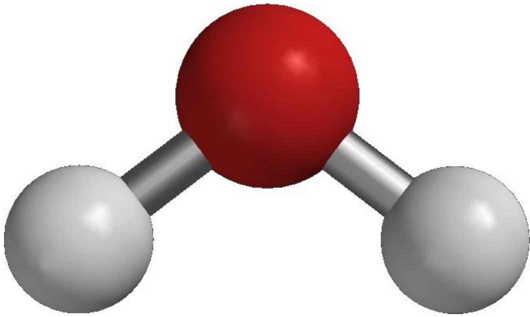


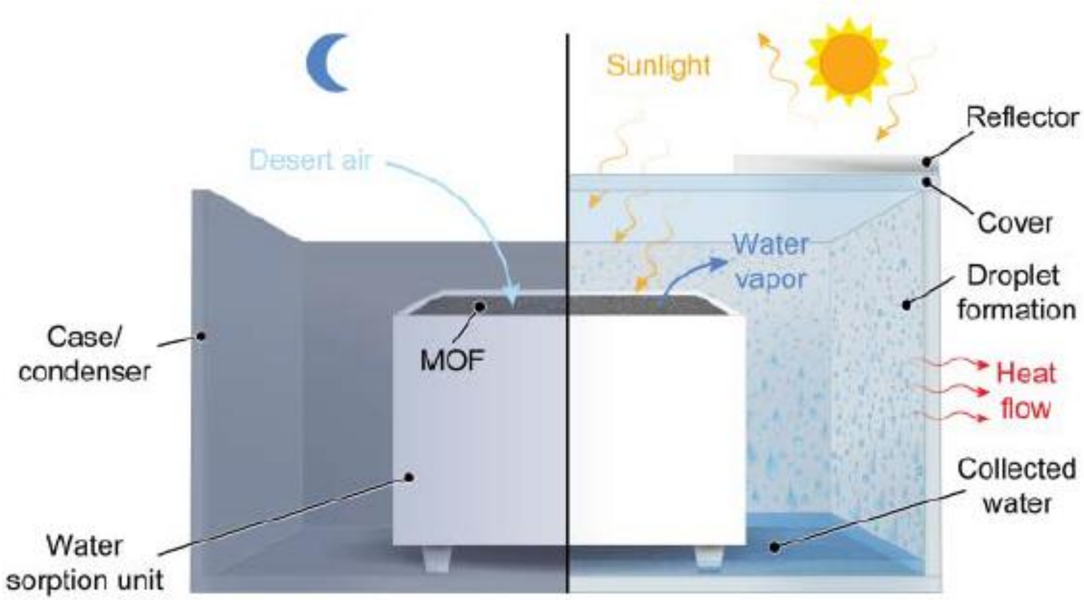
Applications of MOFs





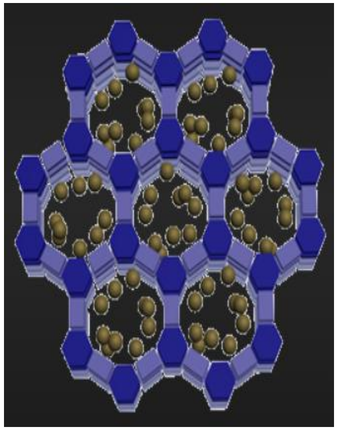


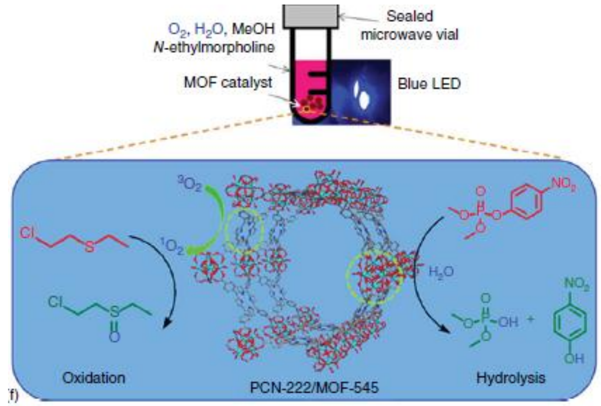


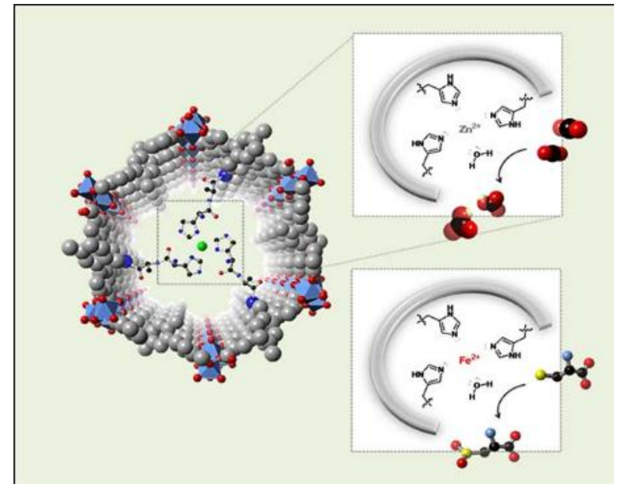


F.Fathieh, M. J. Kalmutzki, E. A. Kapustin, P. J. Waller, J. Yang and O. M. Yaghi, *Science Advances,* **2018,** 4 (6): eaat3198.

Applications of MOFs







•Liquid and Gas Phase separations

•Capture and Degradation of Chemical Warfare Agents

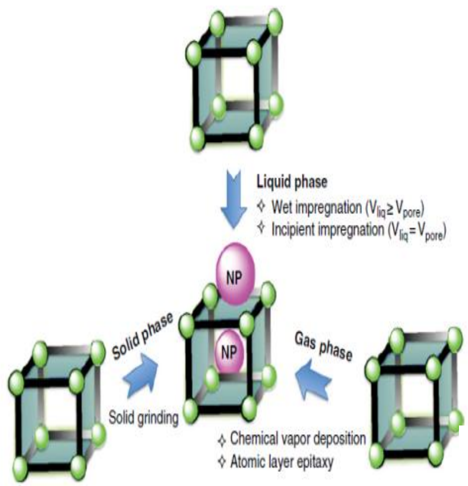
•Catalysis

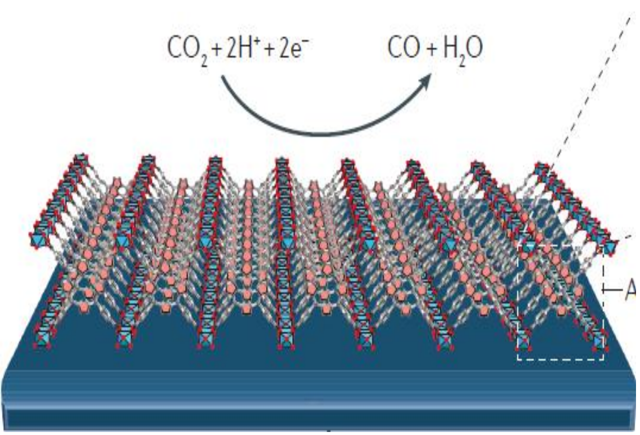
•Drag Delivery

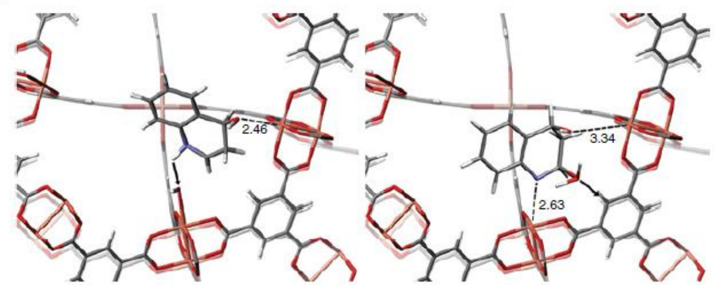
• Sensing

•Air purification

Other applications of MOFs

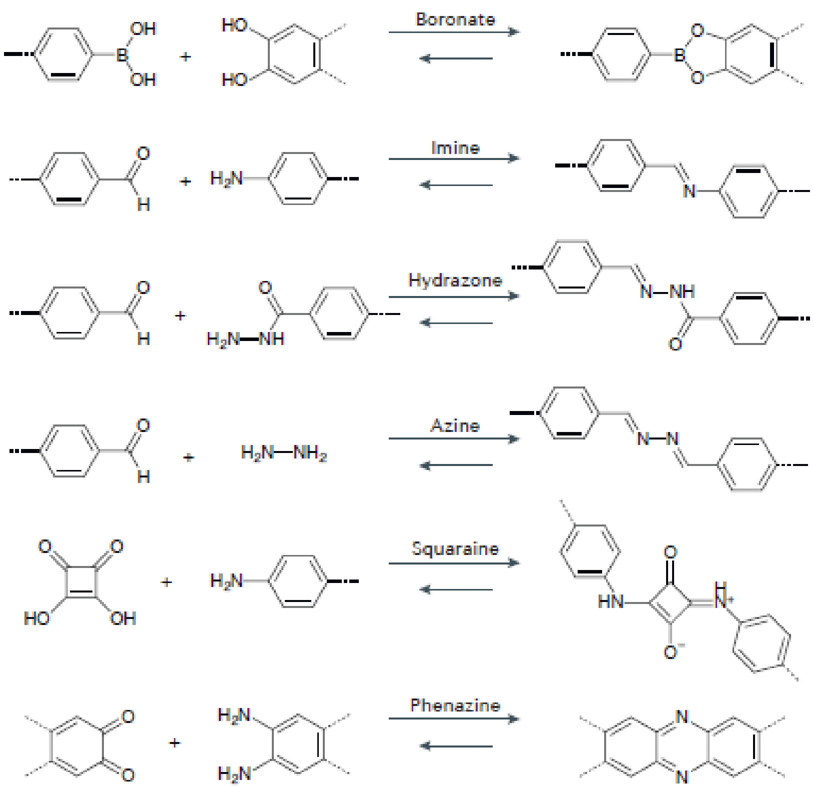


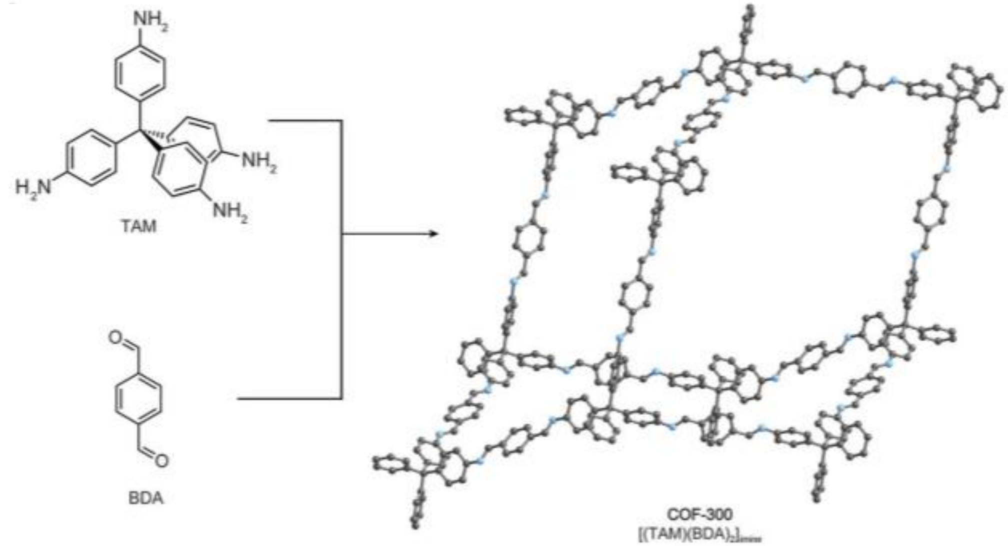


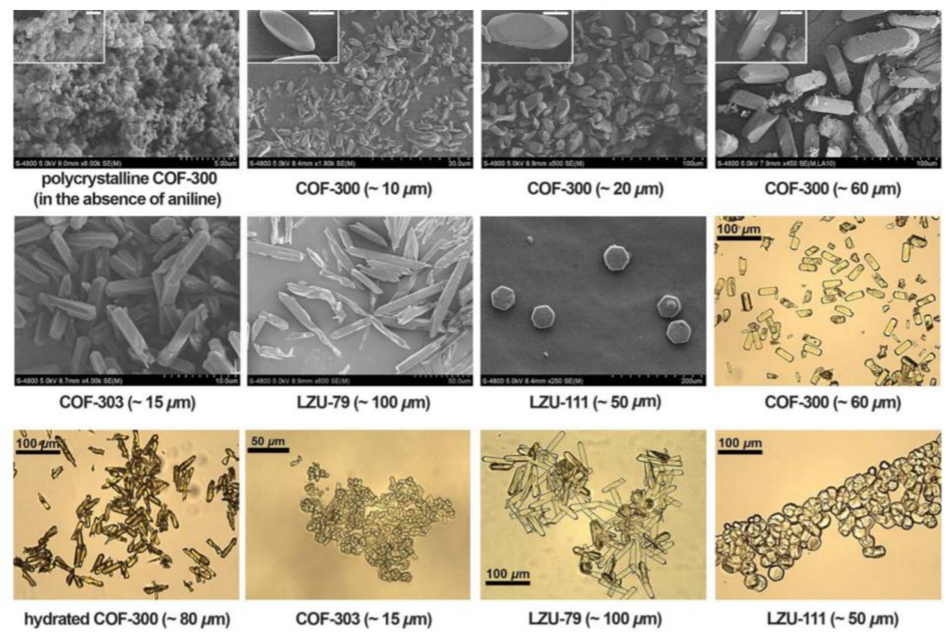


What’s next?

Covalent Organic Frameworks (COFs)







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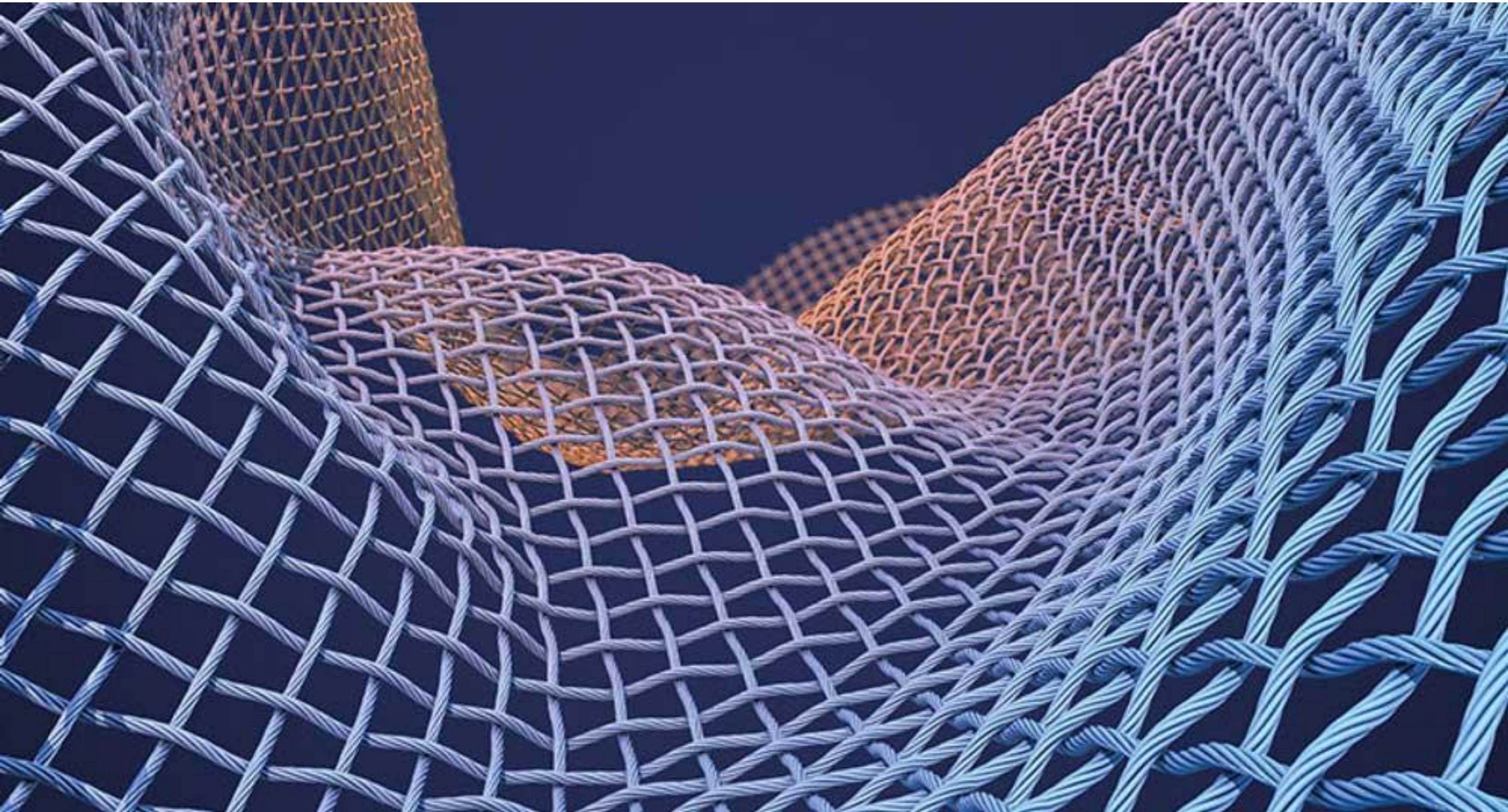
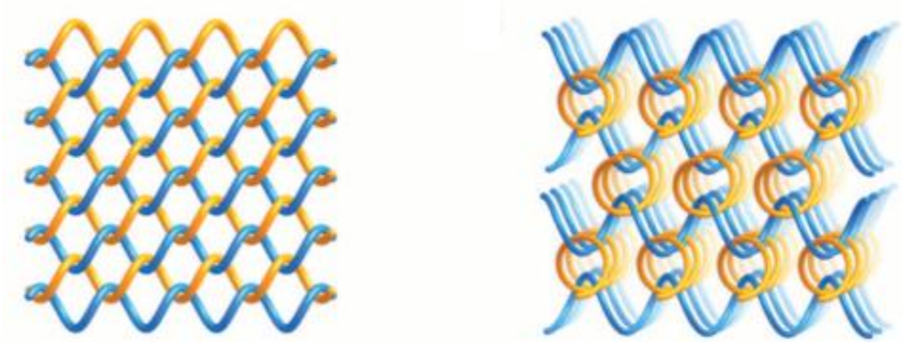
What's next?

Molecular Weaving

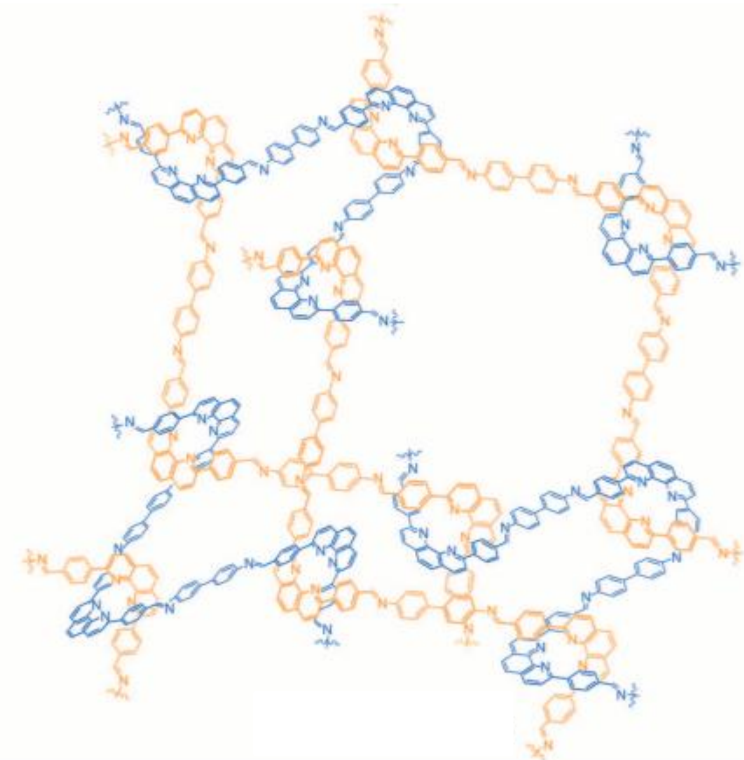


What’s next?

Covalent Organic Frameworks (COFs)



Molecular Weaving



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QUESTIONS