Porous Metal-Organic Frameworks: Emerging Materials for Gas Storage and Separation

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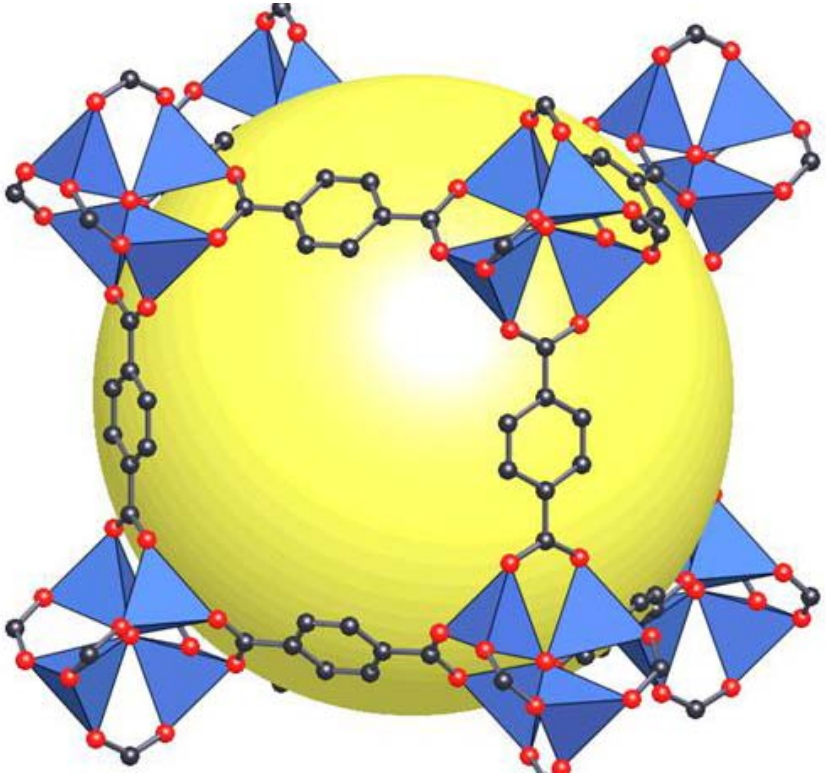
http://www.utsa.edu/chem/chen.html

Breakthrough on Porous MOFs



MOF-5 or IRMOF-1

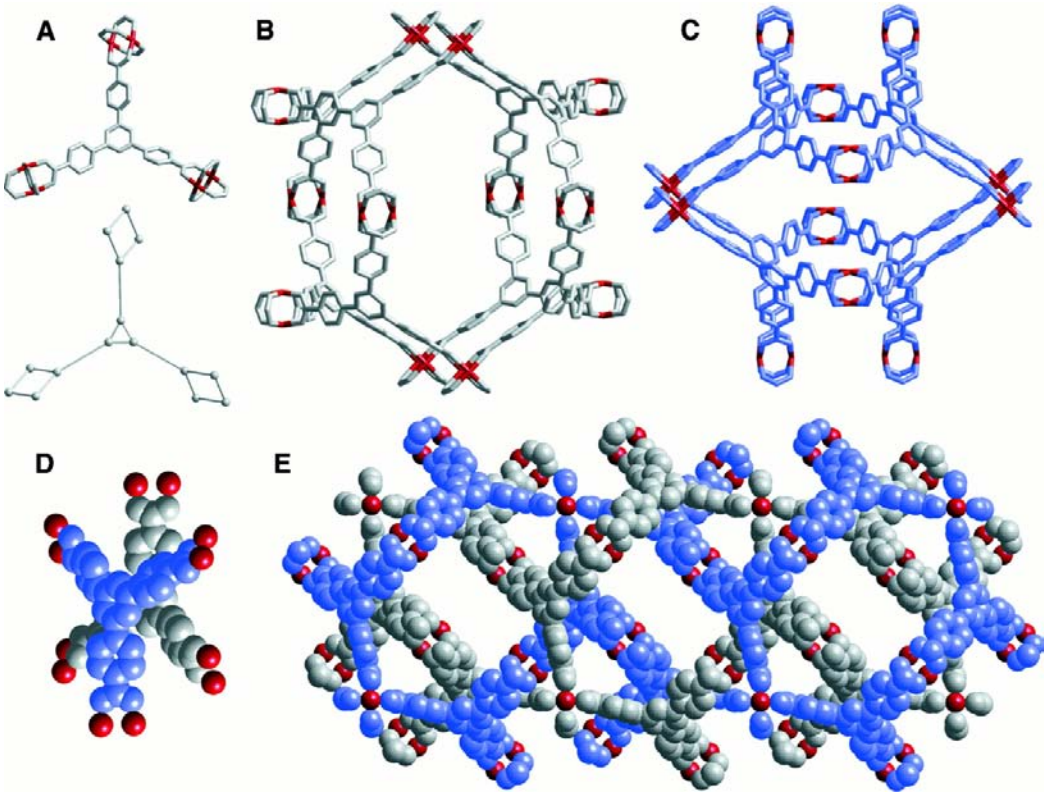
Surface area> 3000 m^2/g

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

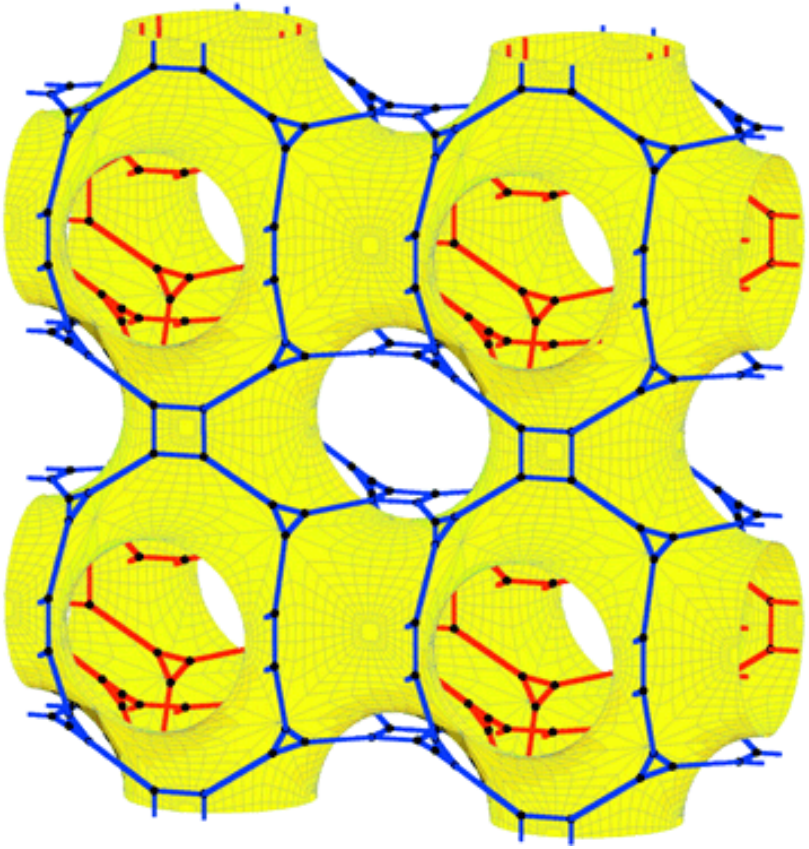
Simple Solvothermal Synthesis and Expanded Organic Linkers for MOFs

$$Cu(NO_3)_2 \cdot 2.5H_2O + H_3BTB \xrightarrow[65\ ^\circ C]{H_2O/EtOH/DMF/Py} Cu_3(BTB)_2(H_2O)_3 \cdot (DMF)_9(H_2O)_2$$

MOF-14



$Cu_3(BTB)_2(H_2O)_3$ Framework with Extra-Large Pores of 16.4 Å



Chen B., Eddaoudi M., Hyde S. T., O'Keeffe M. and Yaghi O. M. *Science* 2001, **291**, 1021.

What they are good for ?

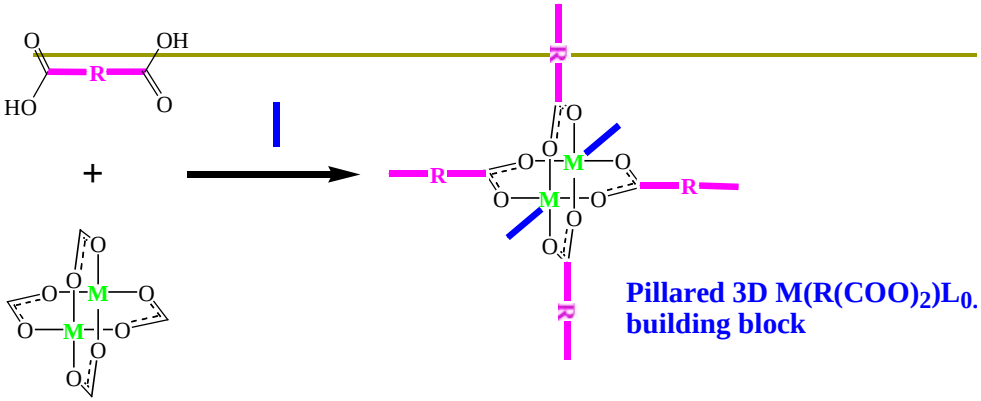
- Functional Pores
- Functional Properties and Practical Applications

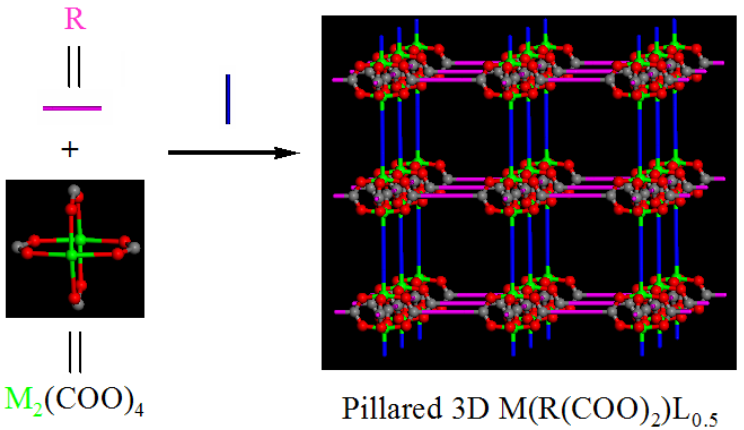
Host (Porous MOF) – Guest (Substrate) Interactions

1. Host-Guest subtle matching confined by pore size/curvature.
2. Specific binding sites (organic and/or metal sites).

Our Approaches

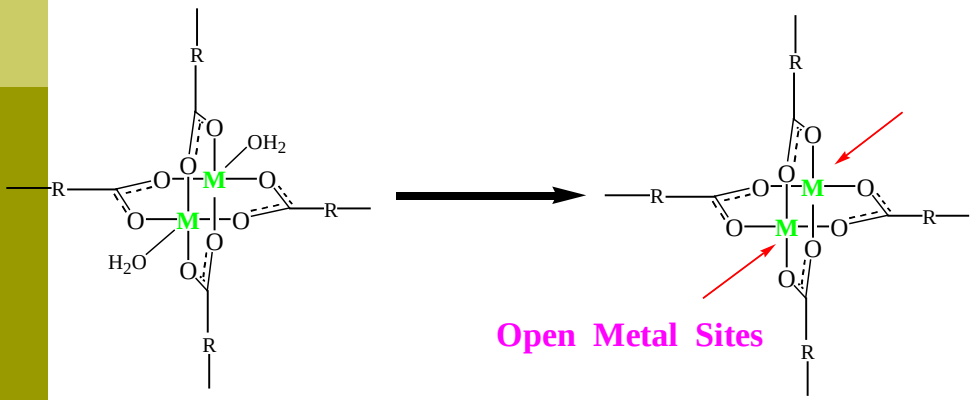
I)





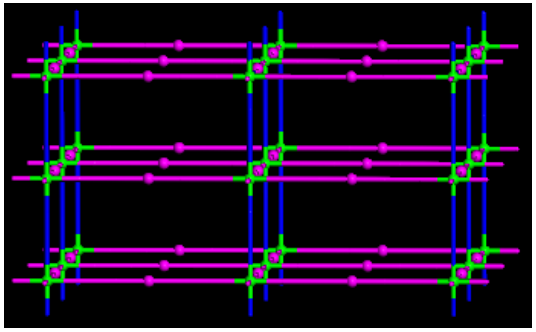
Tunable Micropores

II)



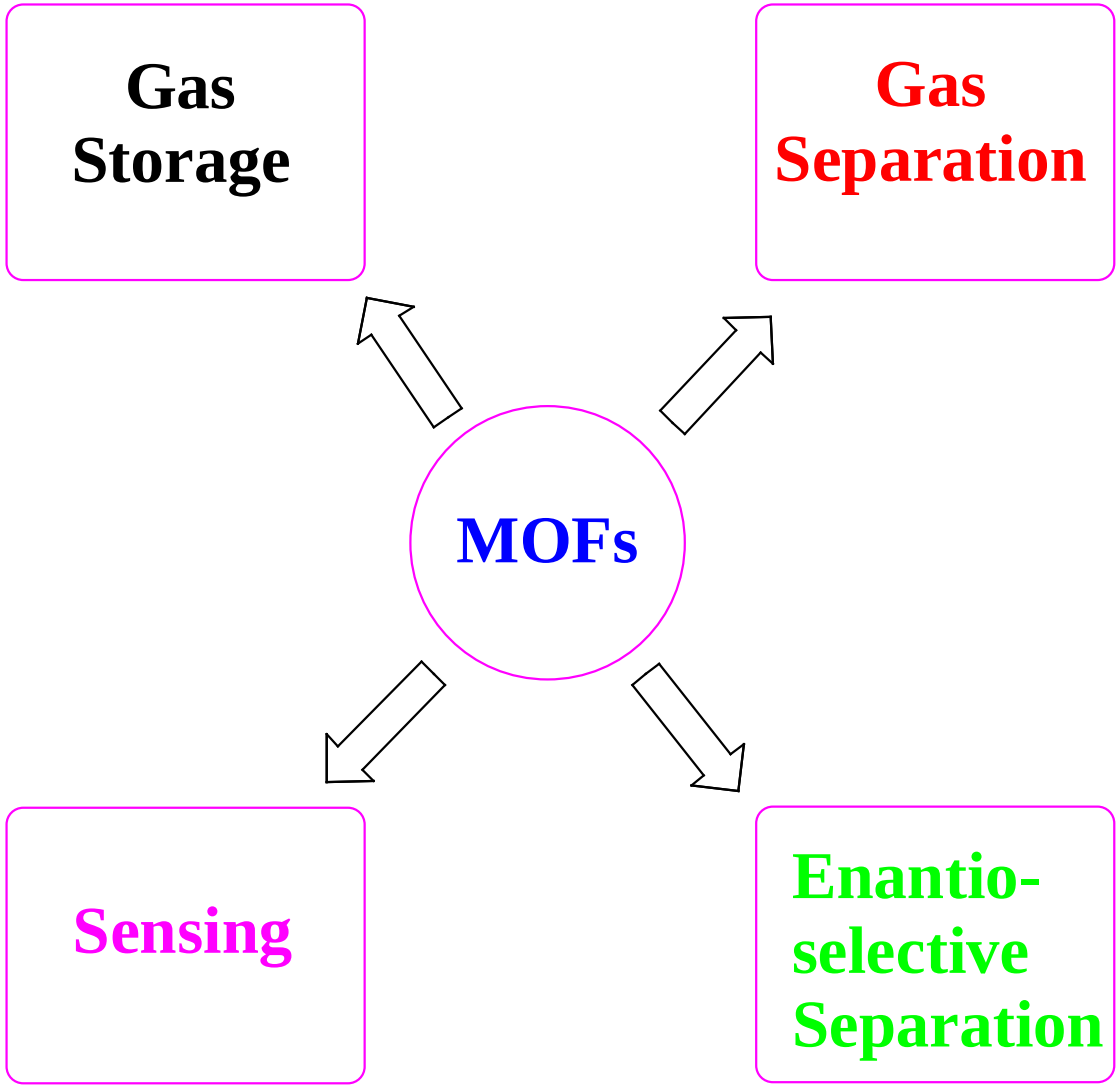
Functional Sites

III)

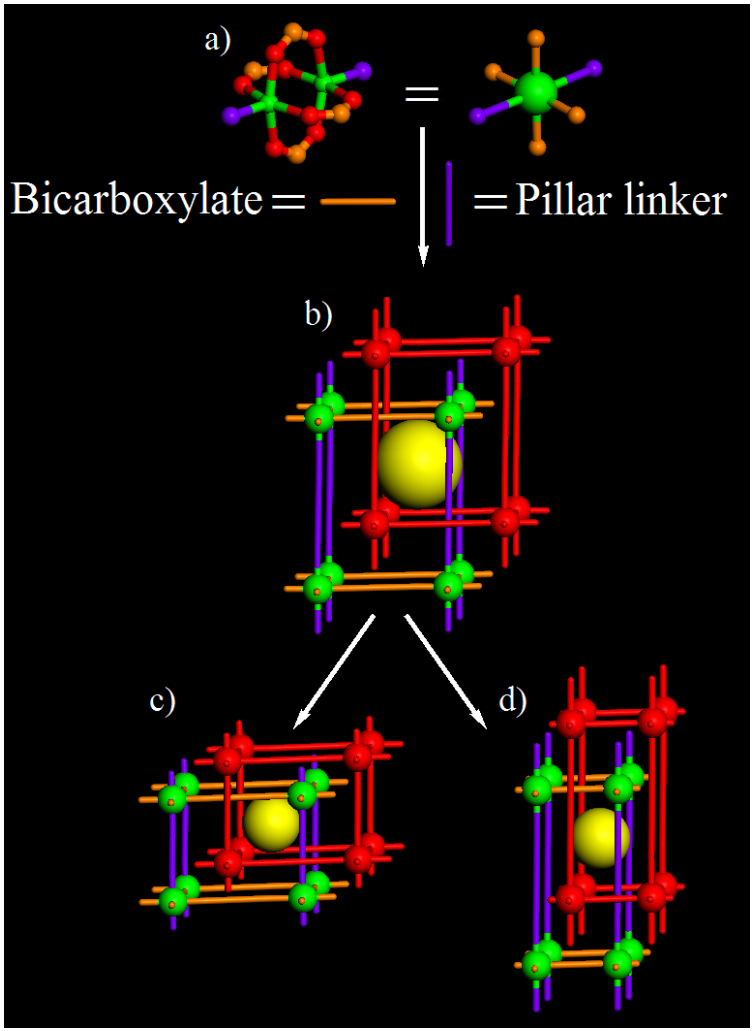


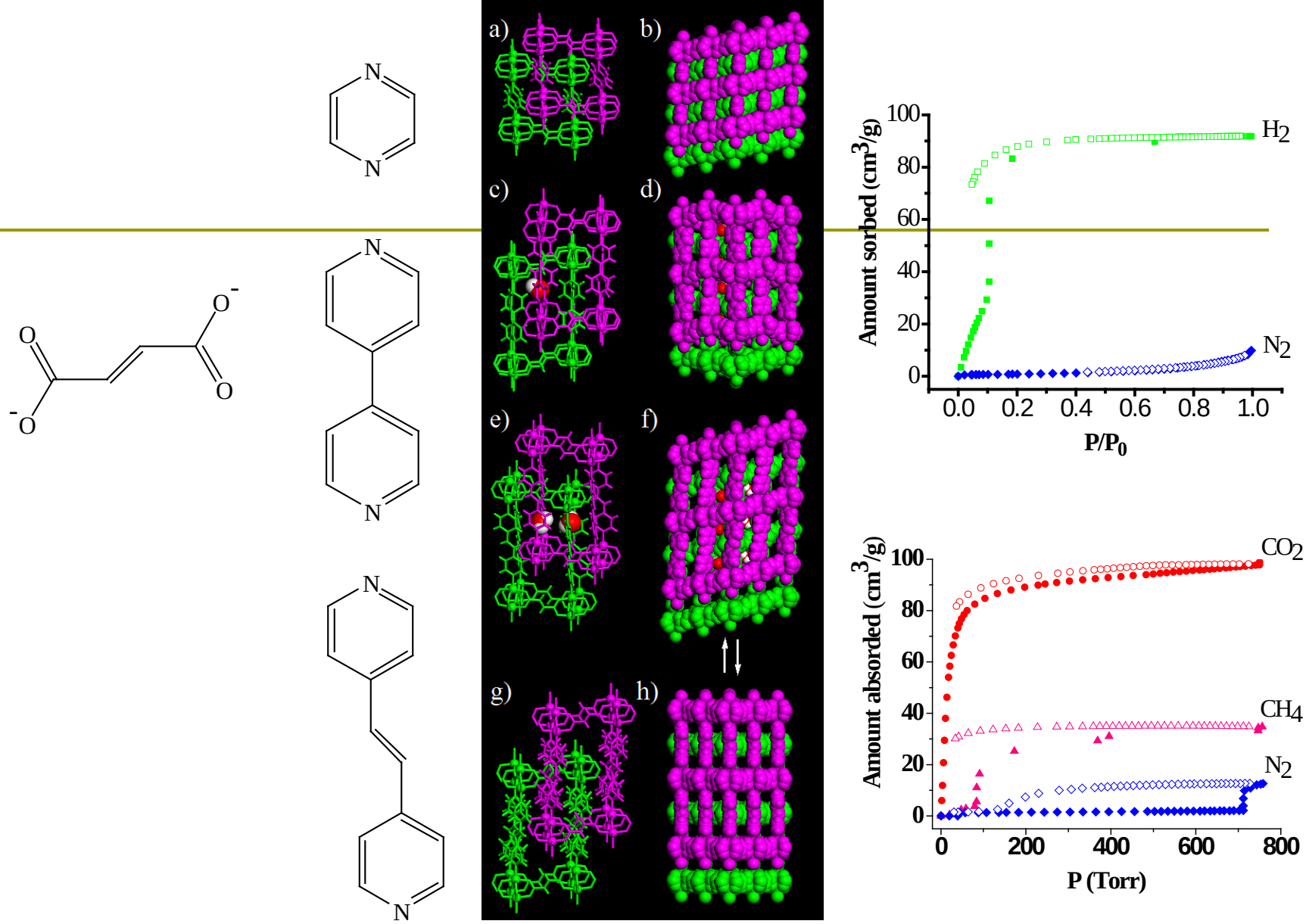
Mixed-Metal-Organic Frameworks

Diverse Functionalities



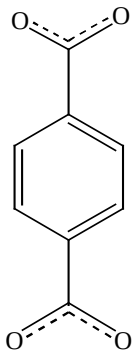
How to tune the pores?

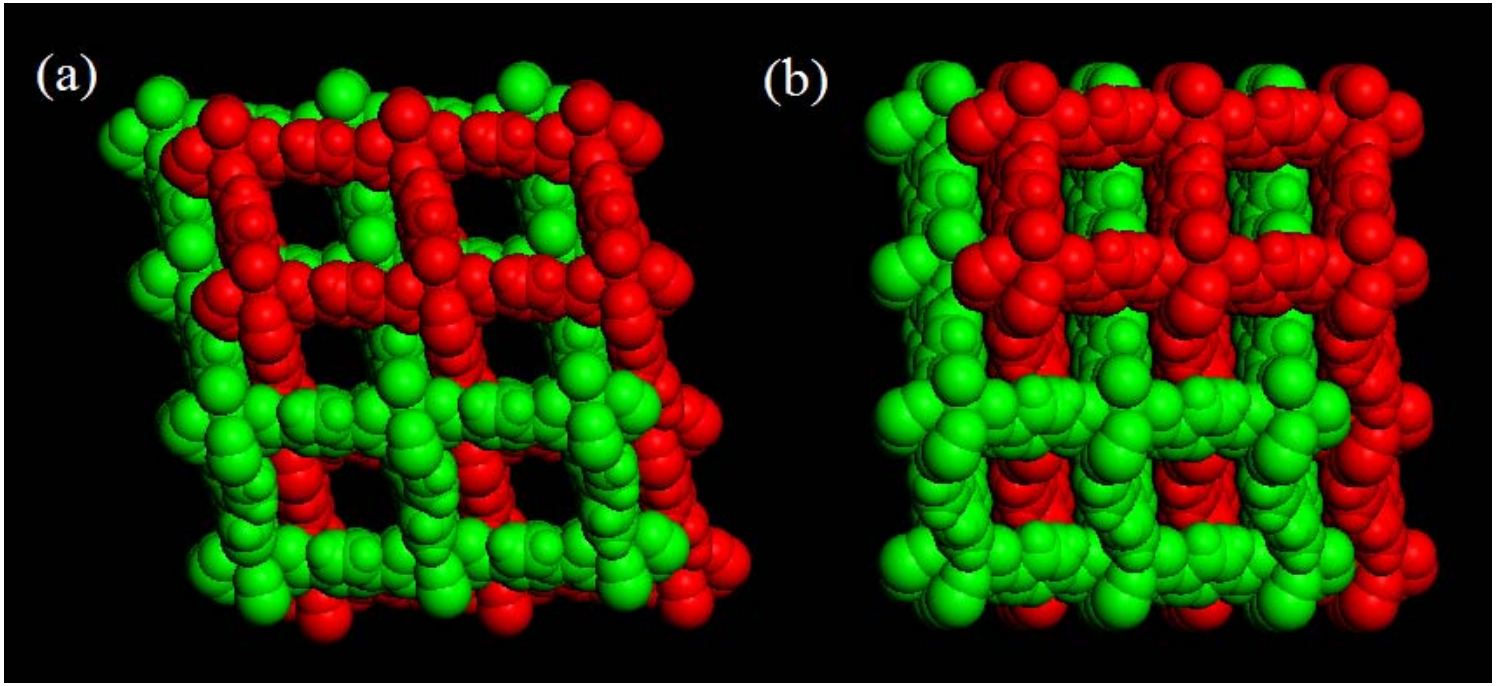


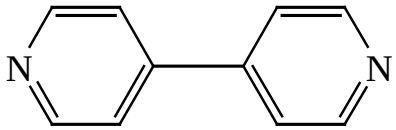


Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou H.-C. *Inorg. Chem.* 2007, **46**, 1233 (SCI citation: 181; most cited paper in *Inorg. Chem.*).

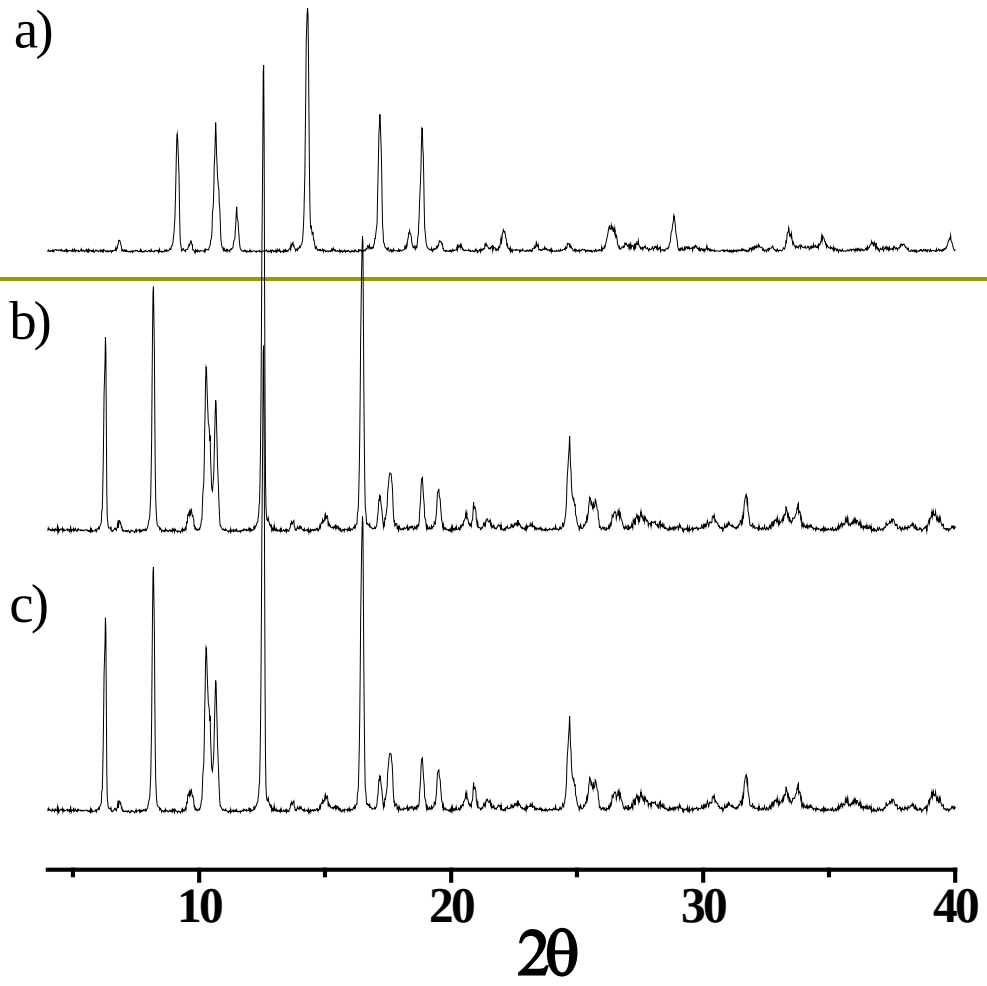
Slightly larger pores and reversible structure transformation







4.0 x 4.0 Å



Powder X-ray diffraction (PXRD) patterns of (a) guest-free dense phase MOF-508b, (b) as-synthesized open phase MOF-508a and (c) regenerated open phase MOF-508a.

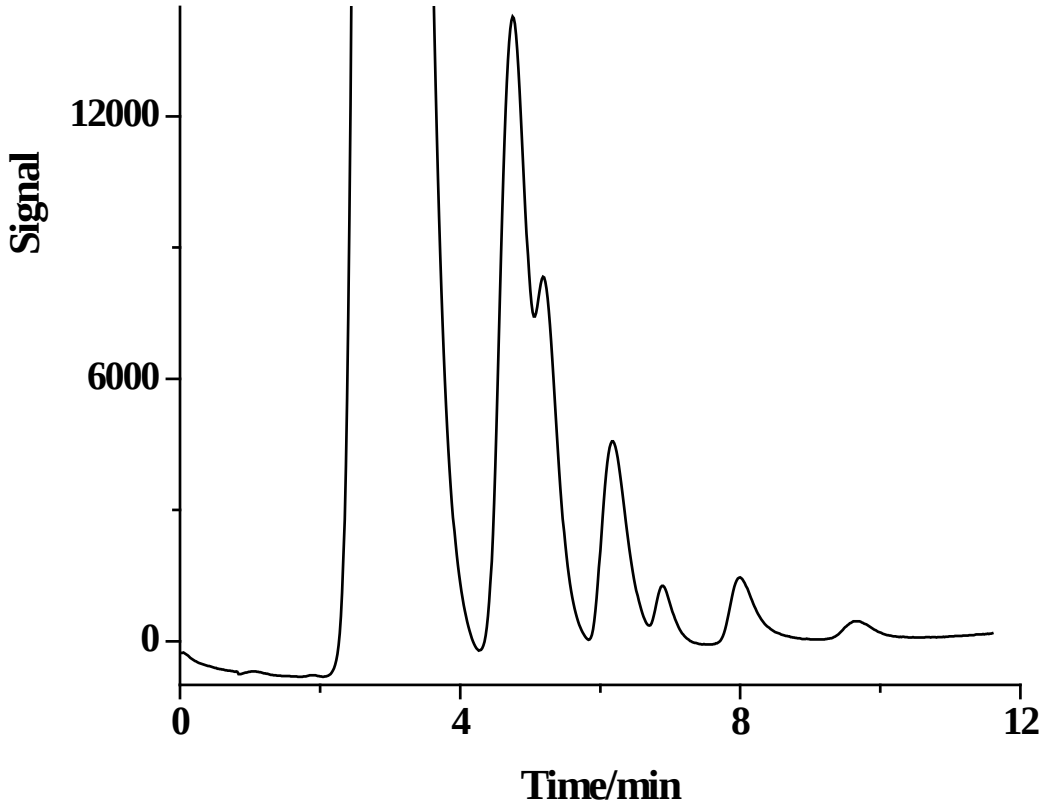
First Microporous MOF for GC Separation of Alkanes

Three Pre-requisites:

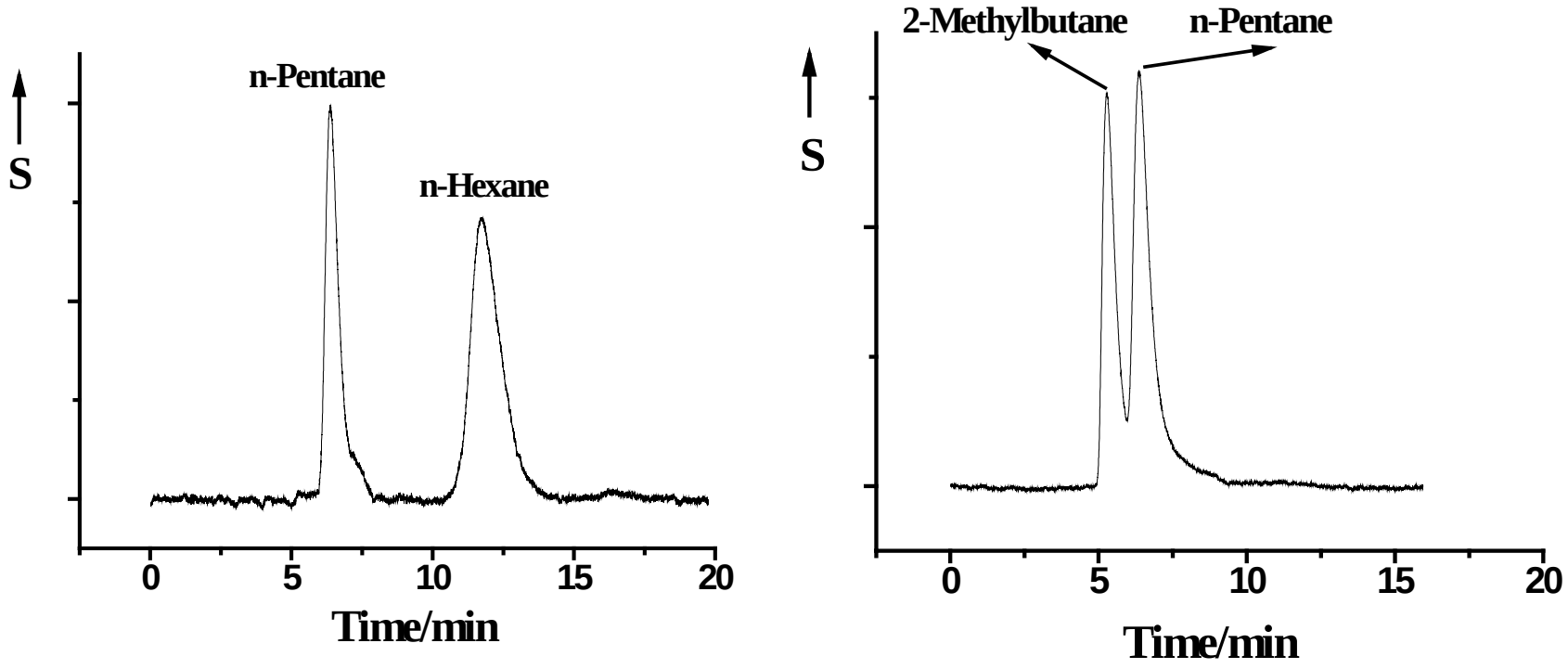
1. Substrate discrimination
2. Suitable Host-Substrate interactions
3. High thermal stability

CH_4 3.8 Å

GC separation of natural gas

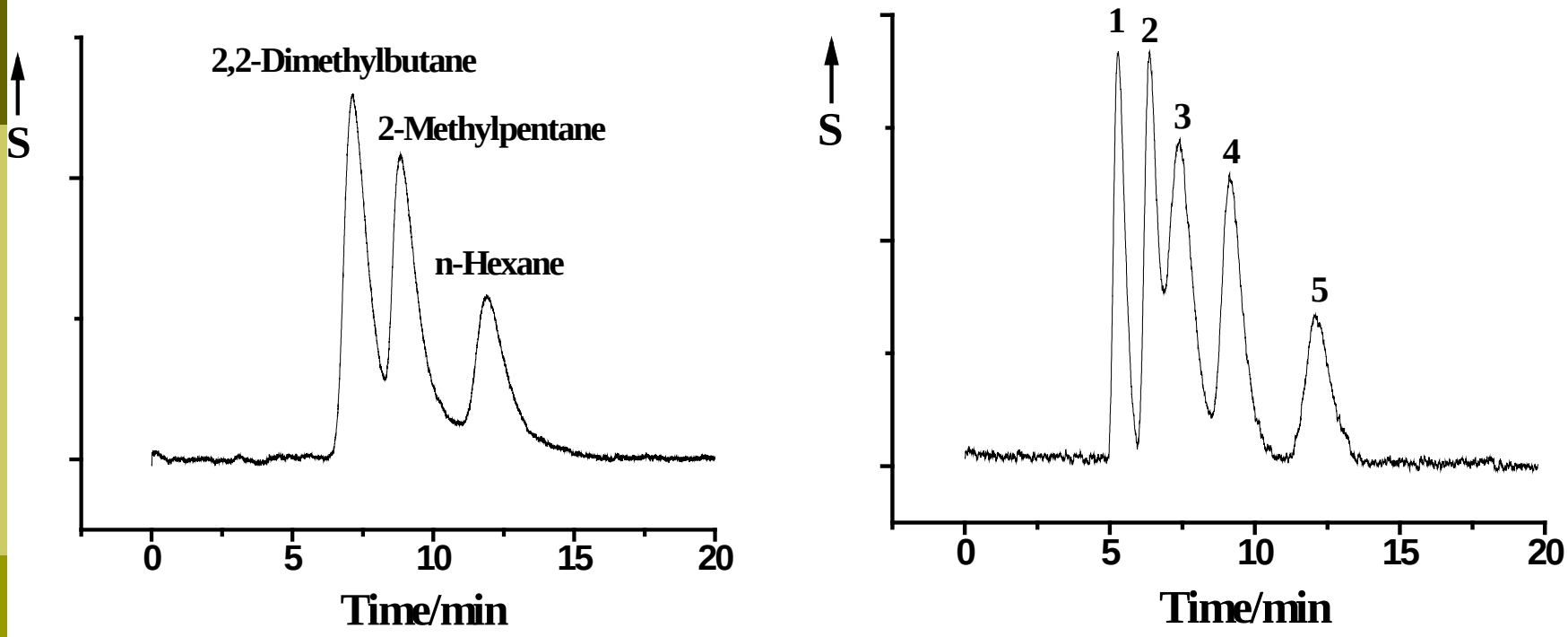


GC Separation of Alkanes



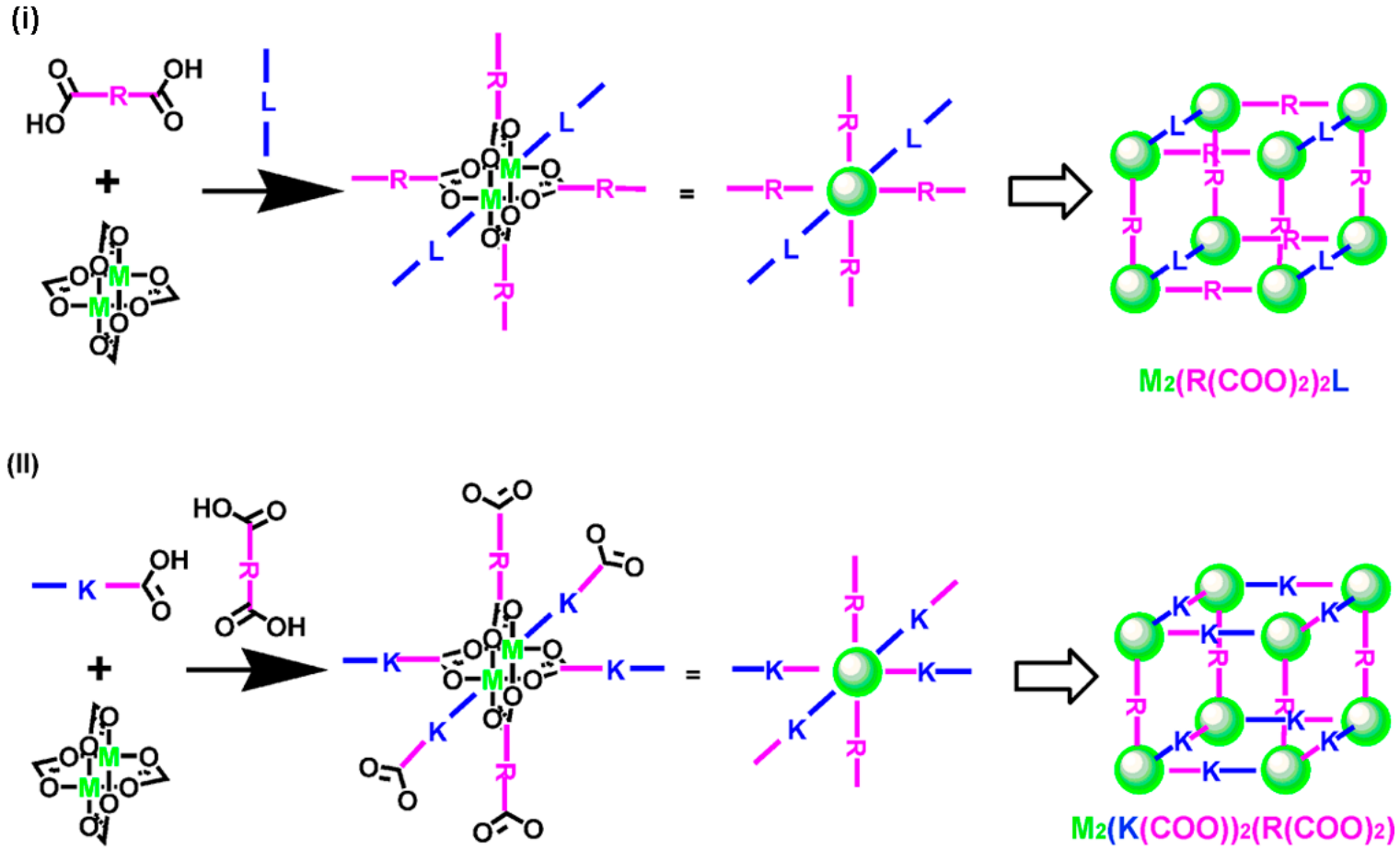
Chen, B.; Liang, C; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem. Int. Ed.*, 2006, **45**, 1390 (SCI citation: 406; most-cited paper; featured to celebrate 50th anniversary of *Angew. Chem. Int. Ed.*).

GC Separation of Alkanes

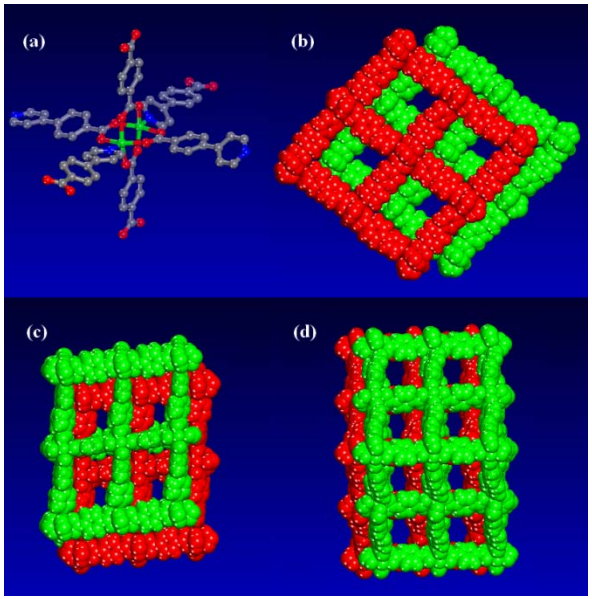


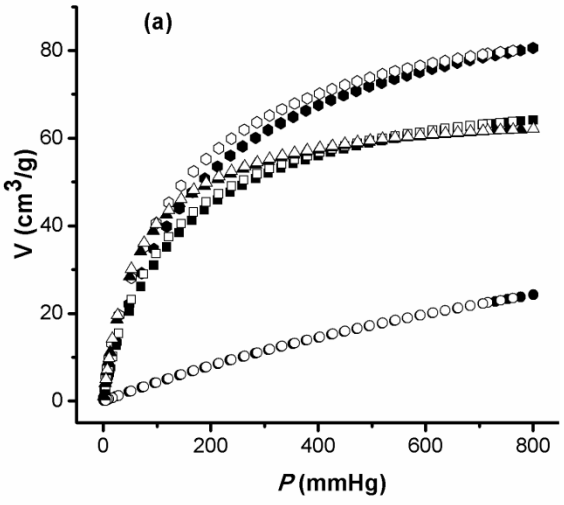
Chen, B.; Liang, C; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem. Int. Ed.*, 2006, **45**, 1390 (SCI citation: 406; most-cited paper, featured to celebrate 50th anniversary of *Angew. Chem. Int. Ed.*).

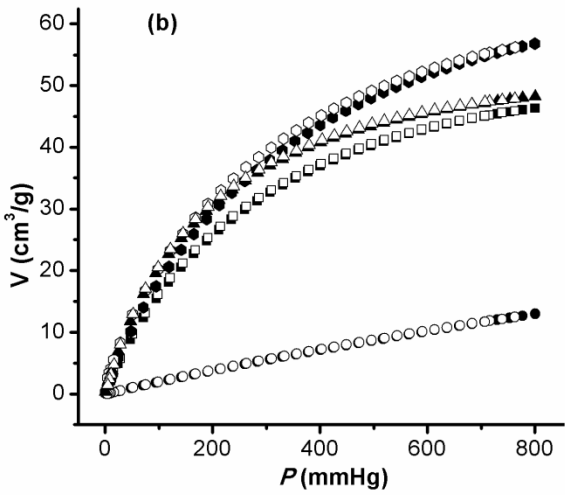
Another Approach to Tune the Micropores



C_1/C_2 Separation

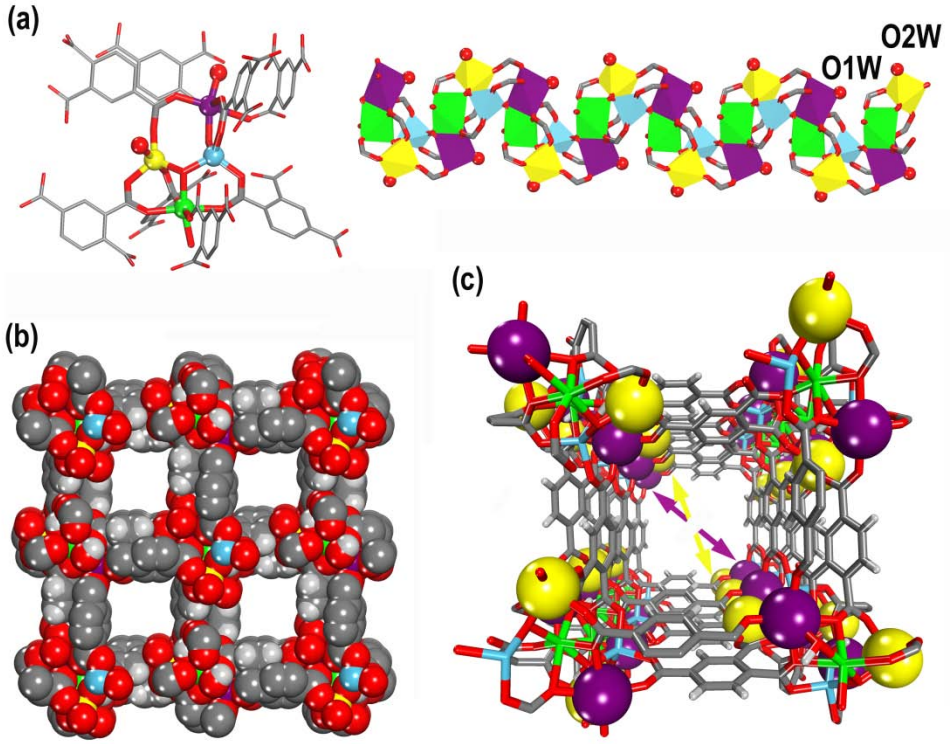


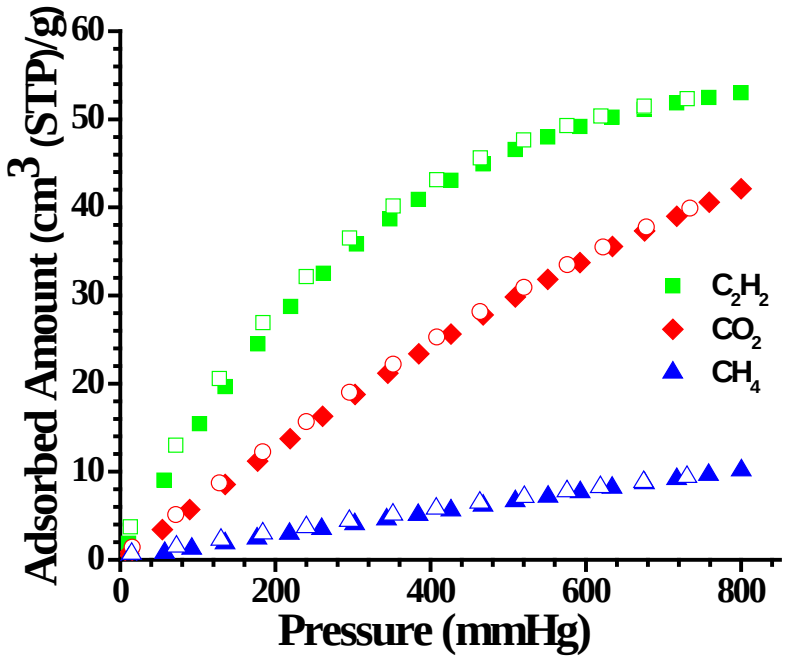




Madhab C. Das, Hui Xu, Shengchang Xiang, Zhangjing Zhang, Hadi D. Arman, Guodong Qian and Banglin Chen, *Chem. Eur. J.* **2011**, *17*, 7817 (VIP paper)

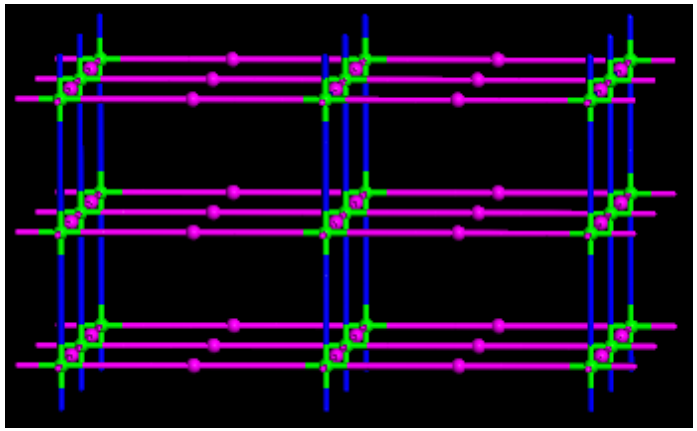
Open Metal Sites for Gas Separation

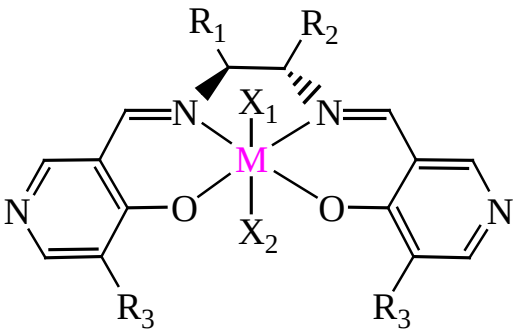




Zhang, Z.; Xiang, S.; Rao, X.; Zheng, Q.; Fronczek, F. R.; Qian, G.; Chen, B. *Chem. Commun.* **2010**, *46*, 7205.

Metalloligands for M'MOFs

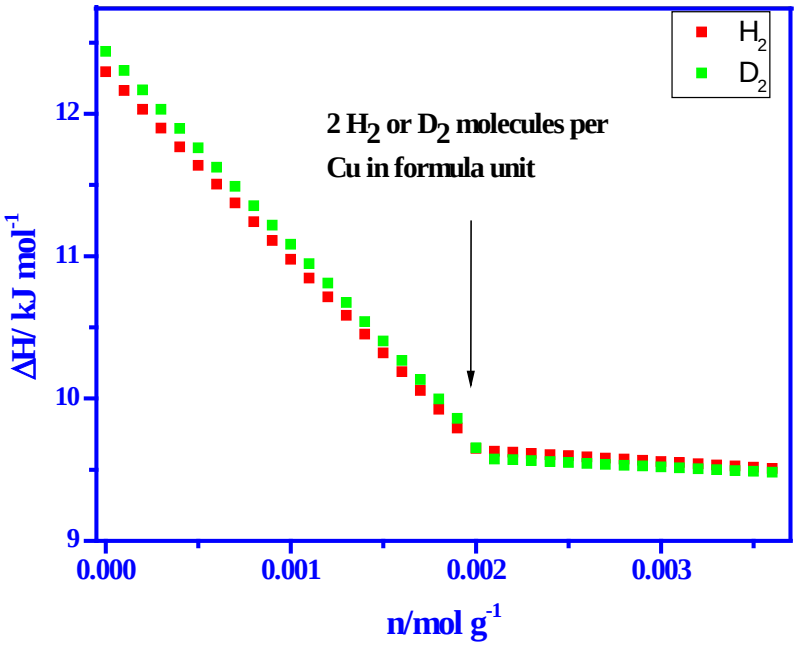




M(Salen-Py)X_1X_2

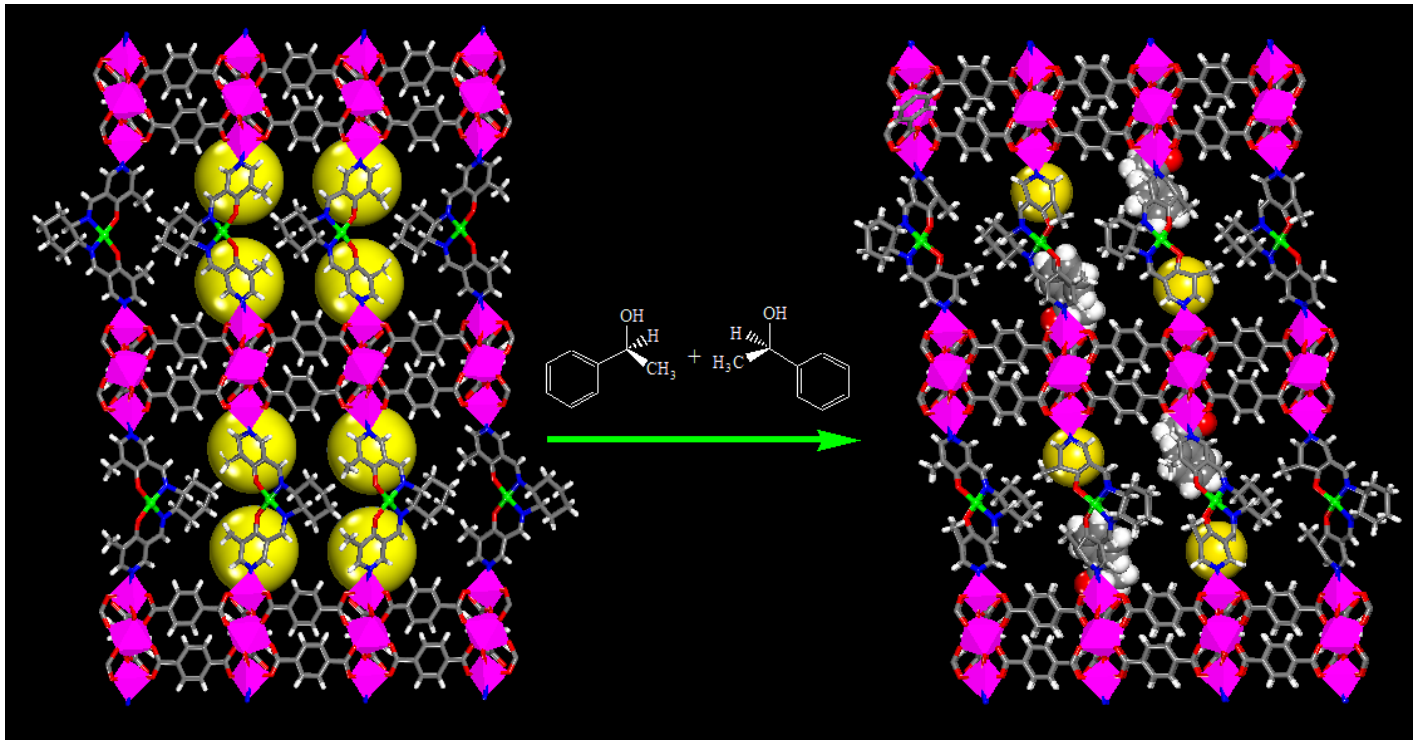
Kunlun Hong, CNMS user program

High Adsorption Enthalpy and Kinetic Separation of H_2/D_2 by a Microporous Mixed-Metal-Organic Framework



Chen B.; Zhao, X.; Putkham, A.; Hong, K.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2008**, *130*, 6411 (SCI citation: 121).

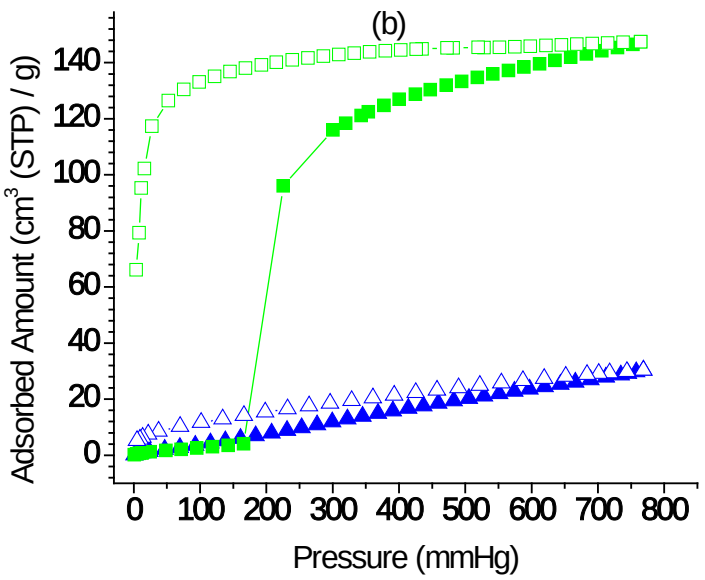
M’MOF for Enantioselective Separation

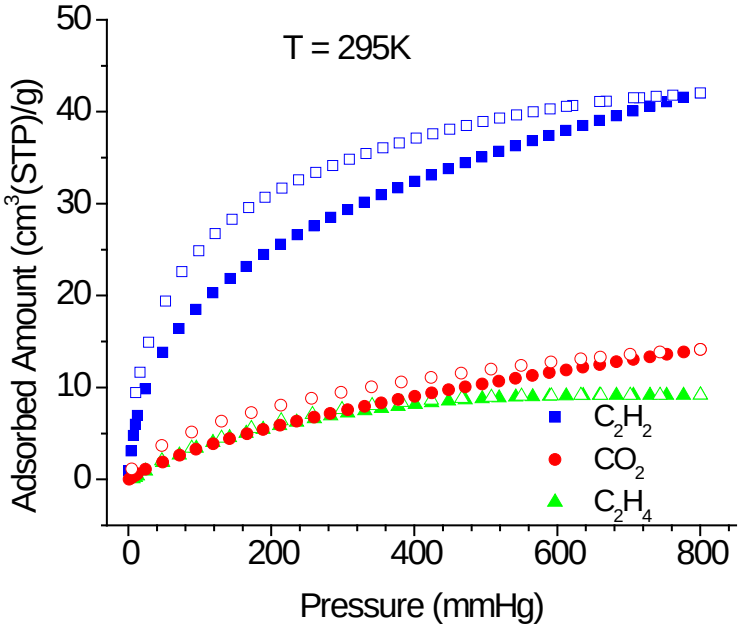


M’MOF⊃G M’MOF⊃S-Phenylethanol

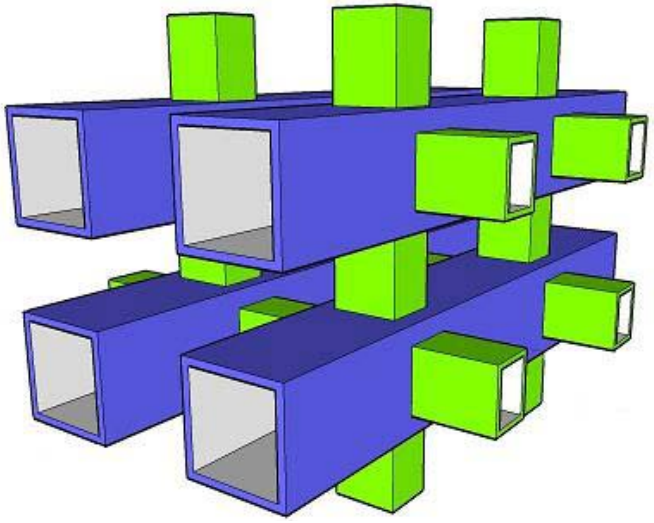
S. Xiang, Z. Zhang, C.-G. Zhao, K. Hong, X. Zhao, D.-R. Ding, M.-H. Xie, C.-D. Wu, M. C. Das, R. Gill, K. M. Thomas, B. Chen, *Nature Communications*, **2011**, *2*, 204.

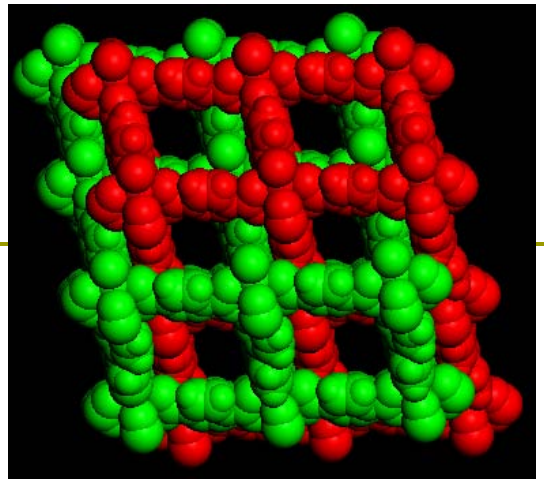
M'MOF for C_2H_2/C_2H_4 Separation

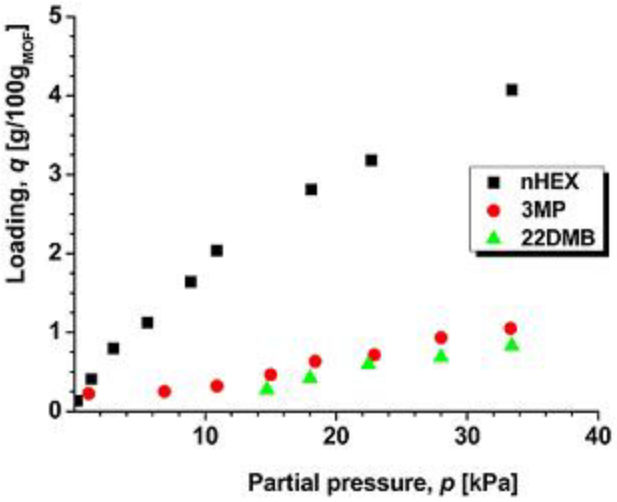


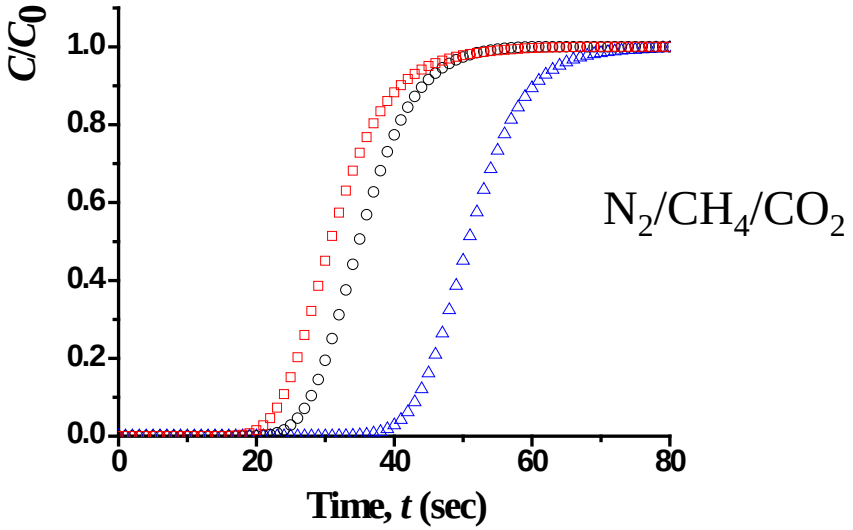


S. Xiang, Z. Zhang, C.-G. Zhao, K. Hong, X. Zhao, D.-R. Ding, M.-H. Xie, C.-D. Wu, M. C. Das, R. Gill, K. M. Thomas, B. Chen, *Nature Communications*, **2011**, *2*, 204.









Bárcia, P. S.; Zapata, F.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. *J. Phys. Chem. B.*, 2007, **111**, 6101.

Bastin, L.; Patrick S. Bárcia, Eric J. Hurtado, Silva, J. A. C.; Rodrigues, A. E.; Chen, B. *J. Phys. Chem. C.*, 2008, **112**, 1575 (SCI citation: 111; most cited paper in JPC).

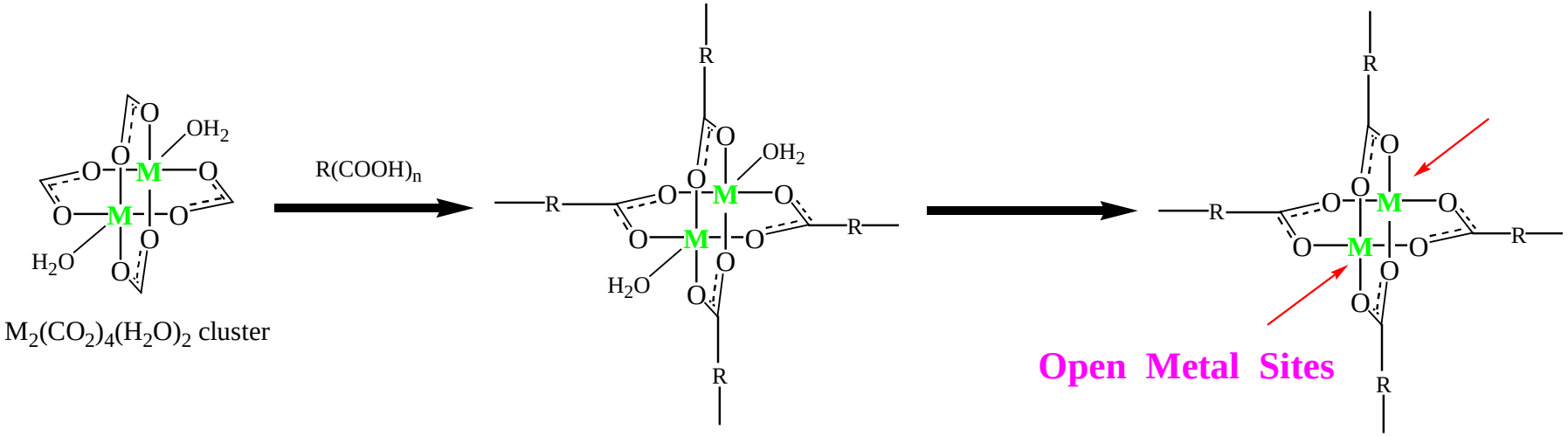
MOFs on Gas Separation

1. Chen, B. *et al. Inorg. Chem.*, **2007**, *46*, 8490.
2. Chen, B. *et al. Inorg. Chem.*, **2007**, *46*, 8705.
3. Chen, B.; Ji, Y.-Y *et al. Inorg. Chem.* **2008**, *47*, 5543.
4. Ming, X.; Ma, S.; Jin, Z.; Schaffino, R. M.; Zhu, G.-S.; Lobkovsky, E. B.; Qiu**,** S.-L.; Chen, B. *Inorg. Chem.* **2008**, *47*, 6825.
5. Chen, Z.; Xiang, S.; Zhao, D.; Chen, B. *Crystal Growth & Design*, **2009**, *9*, 5293.
6. Zhang, Z.; Xiang, S.; Chen, Y.-S.; Ma, S.; Lee, Y.; Phely-Bobin, T.; Chen, B. *Inorg. Chem.* **2010**, *49*, 8444.
7. Chen, Z.; Xiang, S.; Arman, H. D.; Li, P.; Zhao, D.; Chen, B. *Eur. J. Inorg. Chem.* **2010**, 3745.
8. Xue, M.; Zhang, Z.-J.; Xiang, S.; Jin, Z.; Liang, C.; Zhu, G.-S.; Qiu, S.-L.; Chen, B. *J. Mater. Chem.*, **2010**, *20*, 3984.
9. Z. Chen, S. Xiang, H. D. Arman, P. Li, D. Zhao, B. Chen, *Eur. J. Inorg. Chem.* **2011**, DOI: 10.1002/ejic.201100034.
10. Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal P. Li, D. Zhao, B. Chen, *Inorg. Chem.* **2011**, *50*, 3442.
11. D. C. Das, Chen. B. *et al. Chem. Commun.*, **2011**, DOI:10.1039/C1CC12802G.

Hydrogen Storage ?

- High Porosity ($A_{surf} > 1500\ m^2/g$)
- Suitable Pore Size/Curvature
- Functional Pores: Physical + Chemical Hydrogen Adsorption

Microporous MOFs with Open Metal Sites



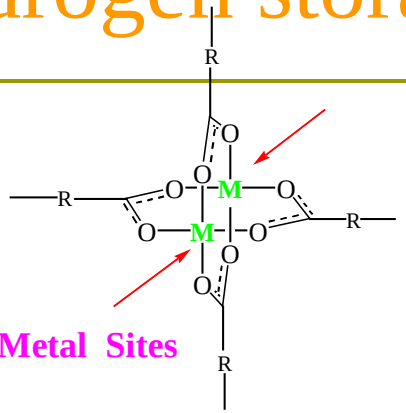
Approach I

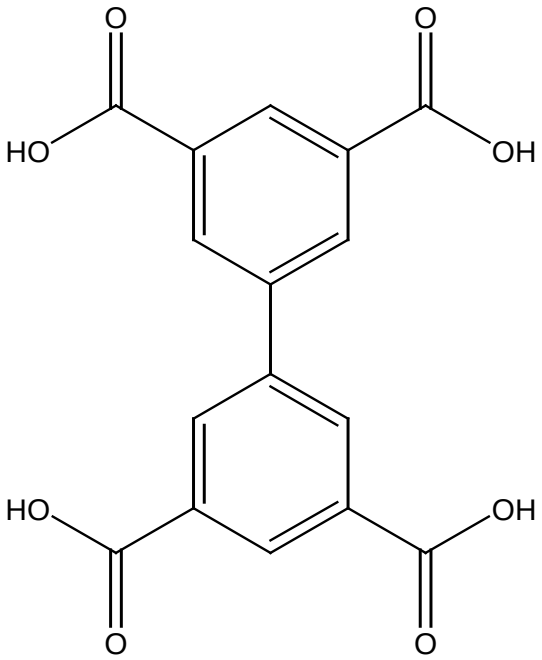
Chen B.; Eddaoudi M. *et al.*, *J. Am. Chem. Soc.* 2000, **122**, 11559.

MOF with open metal sites for hydrogen storage

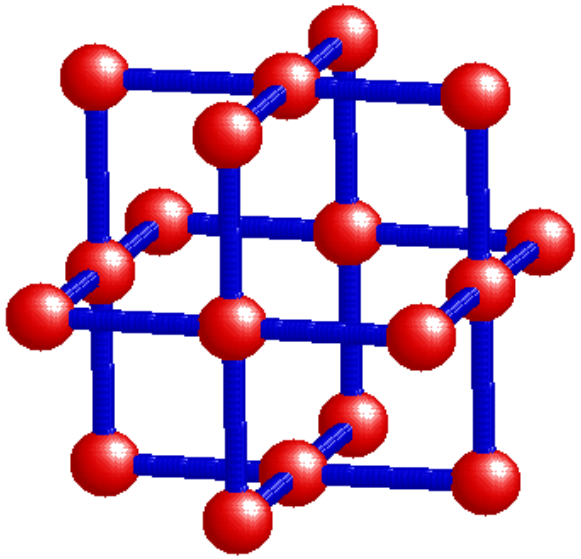
$Cu(NO_3)_2 \cdot 2.5H_2O + H_4BPTC \xrightarrow[65\ ^\circ C]{H_2O/EtOH/DMF} Cu_2(BPTC)(H_2O)_2 \cdot (DMF)_3(H_2O)$

MOF-505

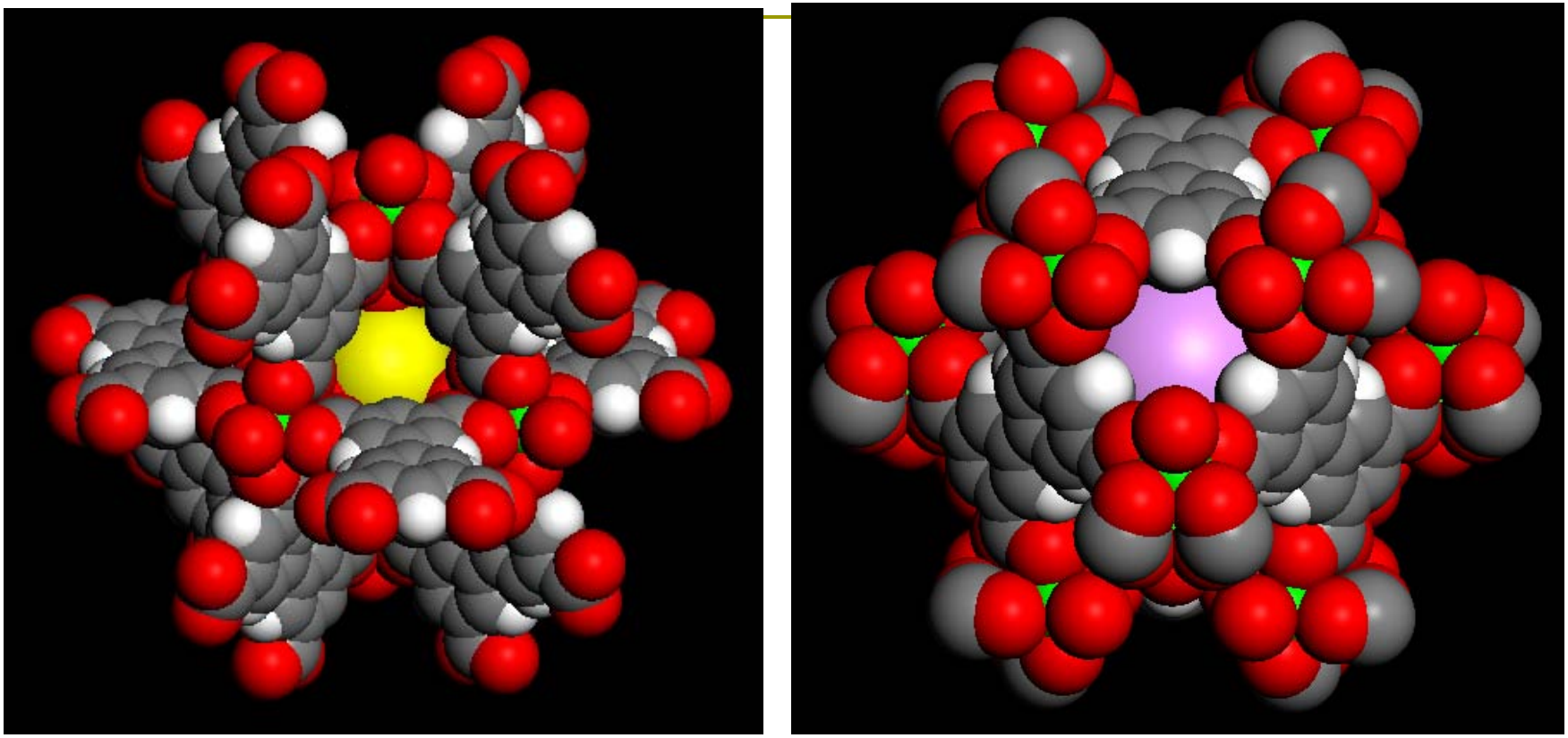




H_4BPTC



Structure of MOF-505



Pores viewed along *c* axis

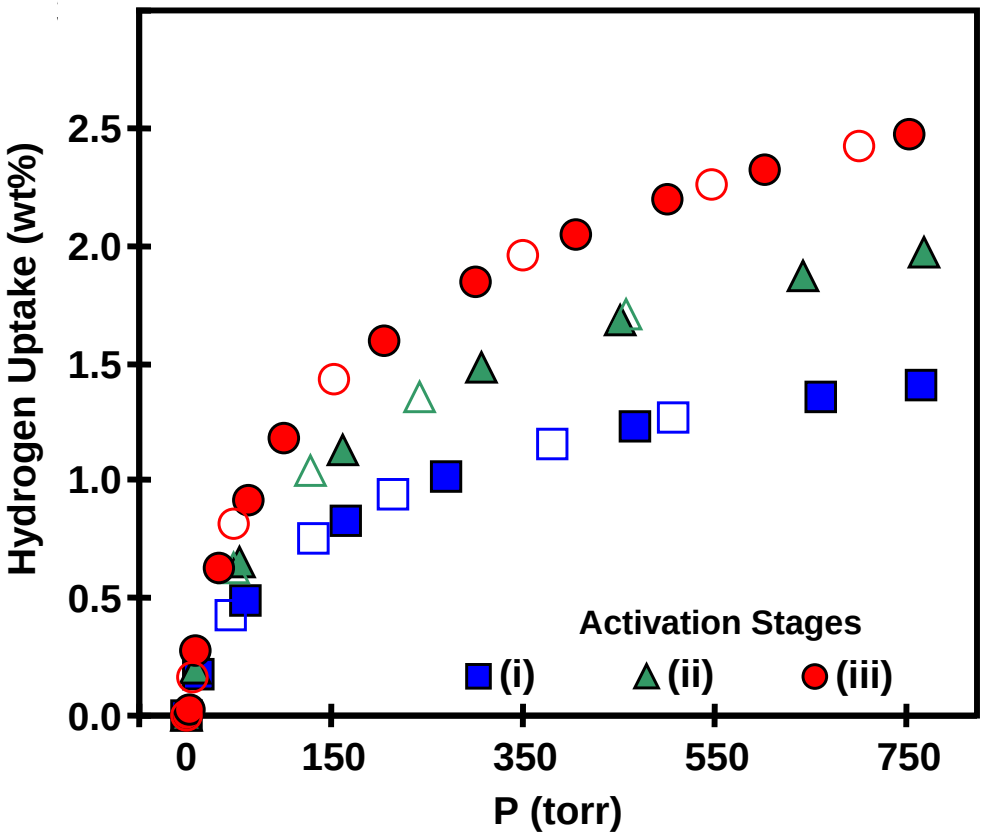
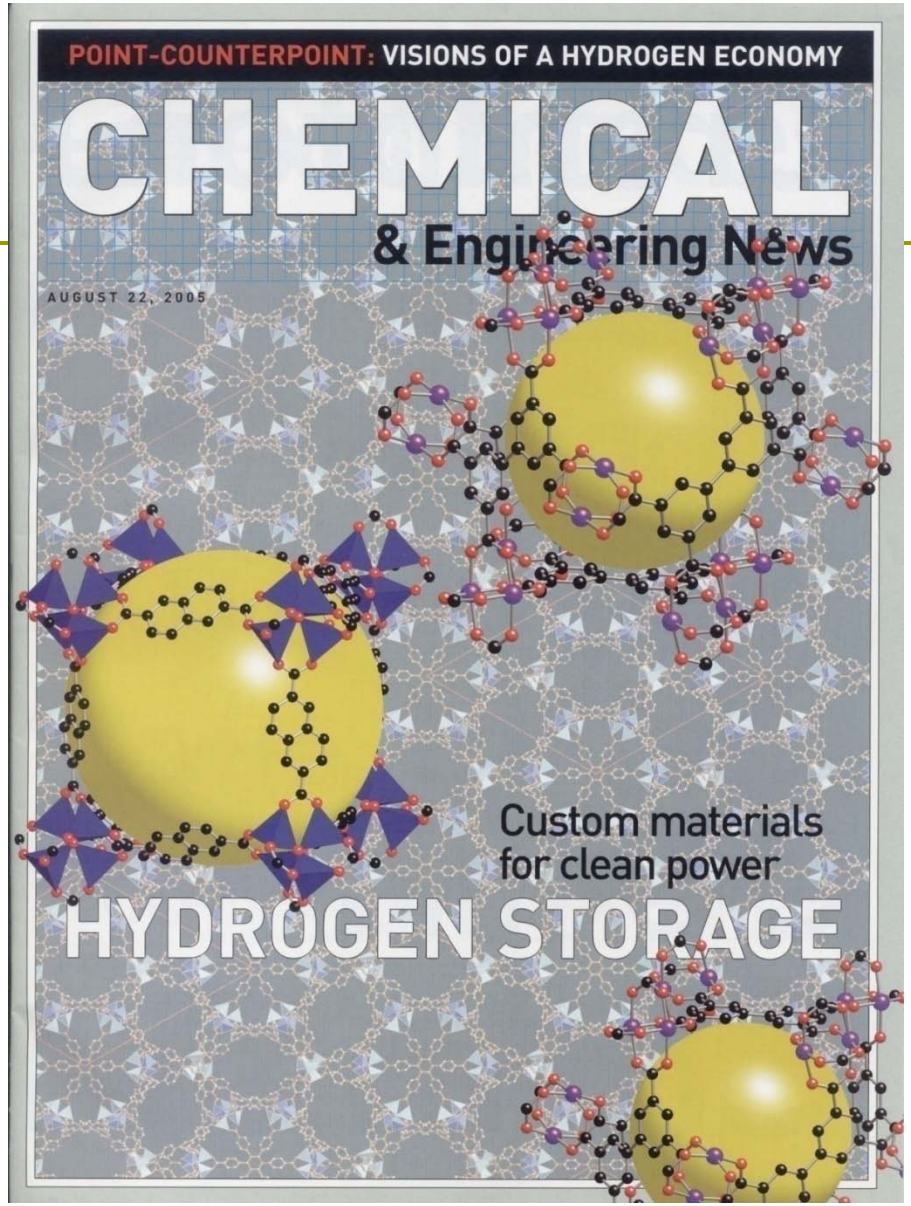
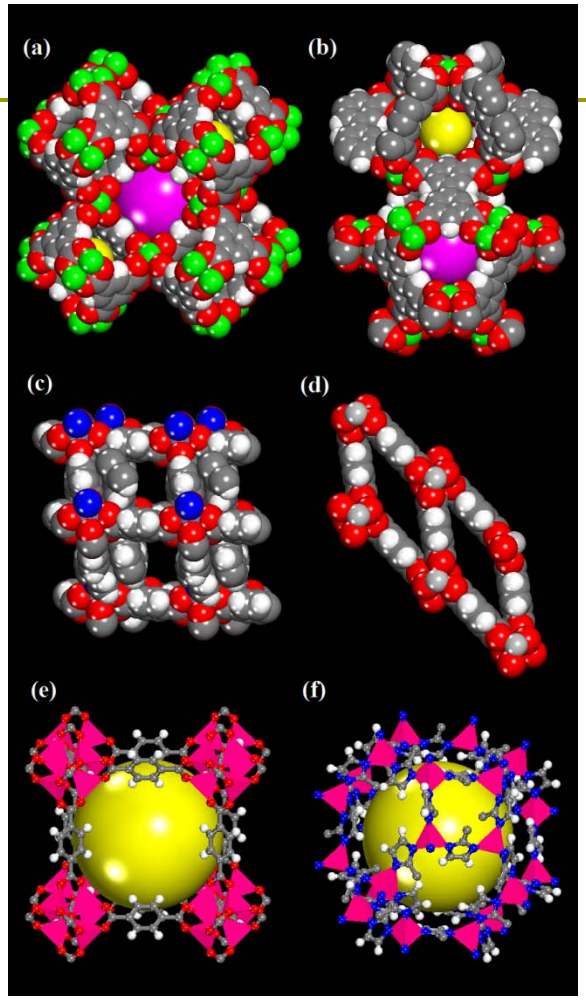


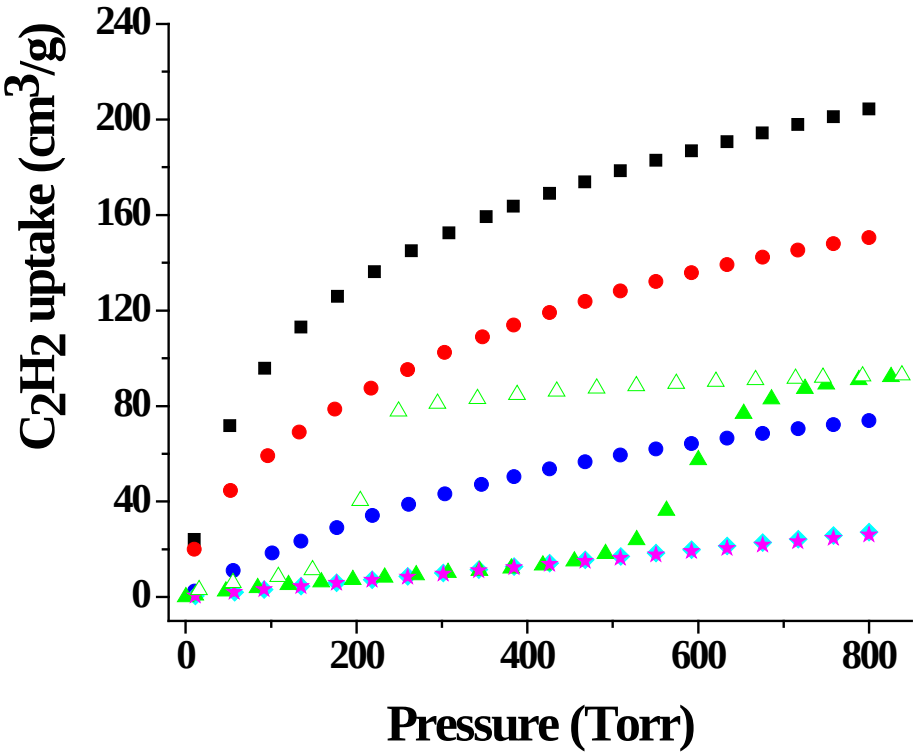
Fig 4. H_2 isotherms for MOF-505 (77 K) after three different activation stages: stage i (25 ºC, blue squares), stage ii (70 ºC, green triangles) and stage iii (120 ºC, red circles), with hydrogen uptake of 14.1, 19.7 and 24.7 mg/g respectively.

Chen B.; Ockwig, N. W.; Contreras, D. S.; Millward, A. R.; Yaghi, O. M. *Angew. Chem. Int. Ed.*, 2005, **44**, 4745 (SCI citation: 420; most cited paper in *Angew. Chem.* 2005; Highlighted in the Cover of *Angew. Chem.* , Materials Today and C&E News; Hot Paper in Chemistry; Patent licensed to a multinational company; featured to celebrate 50th anniversary of *Angew. Chem. Int. Ed.*).


POINT-COUNTERPOINT: VISIONS OF A HYDROGEN ECONOMY
CHEMICAL
& Engineering News
AUGUST 22, 2005
Custom materials
for clean power
HYDROGEN STORAGE

Acetylene Storage





(a) HKUST-1; (b) MOF-505; (c) MOF-508; (d) MIL-53; (e) MOF-5; (f) ZIF-8

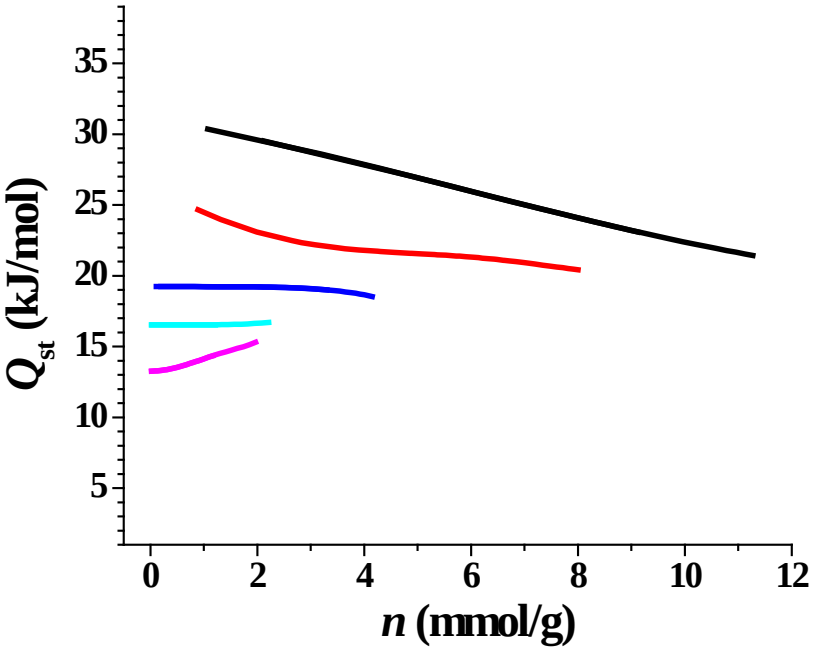
Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc.*, **2009**, *131*, 12415.

Acetylene Storage

Table 1. Acetylene uptake in the six metal-organic frameworks at 295 K and 1 atm (MOF-508 at 290 K).

MOFs (Langmuir surface area, m^2/g)	cm^3/g	$cm^3/cm^{3[a]}$	wt%	Density[b] (g/cm^3)	*P*[c] [MPa]
HKUST-1 (2095)	201	177	23.4	0.21	19.3
MOF-505 (1694)	148	137	17.2	0.16	15.0
MOF-508 (946)	90	112	10.5	0.13	12.2
MIL-53 (1233)	72	67	8.4	0.08	7.3
MOF-5 (3610)	26	15	3.0	0.02	1.6
ZIF-8 (1758)	25	23	2.9	0.03	2.5

Why?



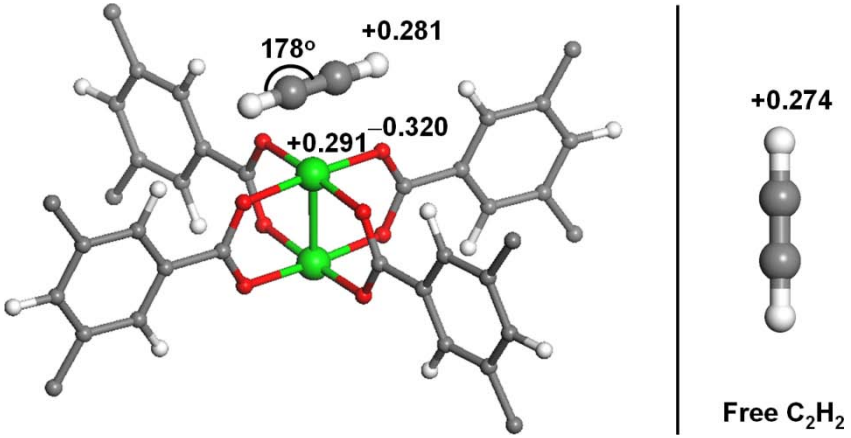


Figure 1 Coverage dependencies of the adsorption enthalpies for C_2H_2 in MOFs calculated from fits of their 273 and 295 K isotherms. HKUST-1 (black); MOF-505 (red); MIL-53 (blue); MOF-5 (cyan) and ZIF-8 (magenta).

Figure 2 The projected Löwdin charges of the C_2H_2 molecule adsorbed on the open Cu^{2+} site in HKUST-1.

Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc.*, **2009**, *131*, 12415.

Where are the Acetylene Molecules?

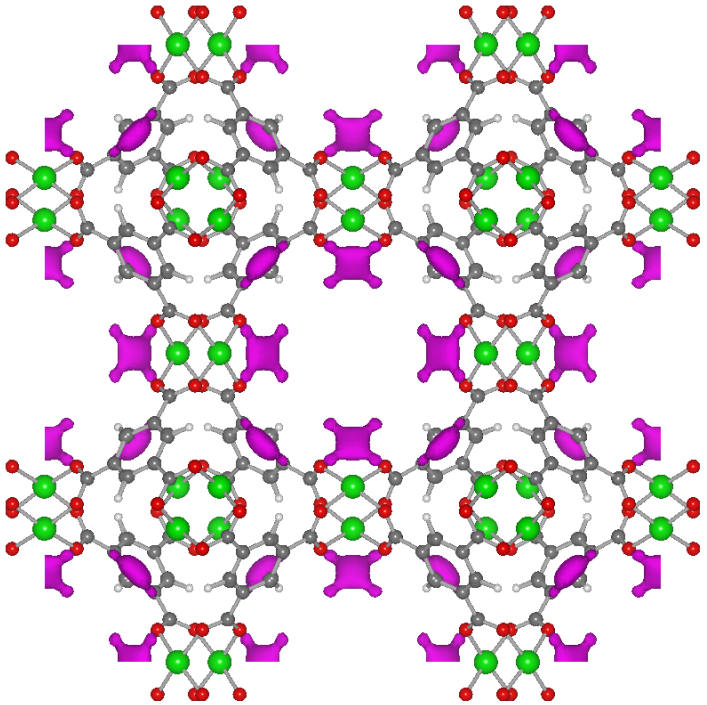


Figure 3 The positive difference Fourier map of 0.62 C_2D_2 per Cu loaded HKUST-1 calculated from powder neutron diffraction data. The pink regions indicate the extra positive density of the adsorbed C_2D_2 molecules bound to the first strongest adsorption sites of open Cu^{2+}

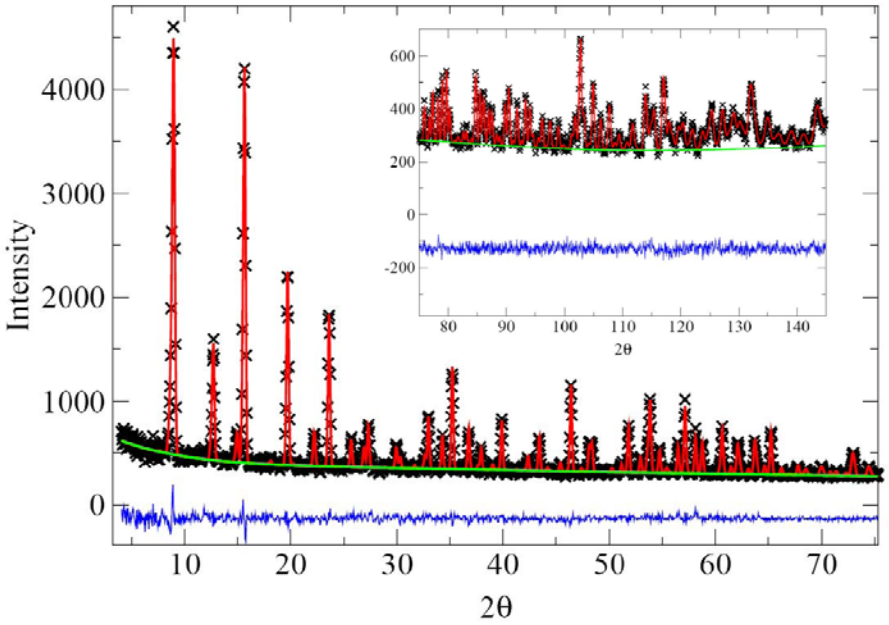
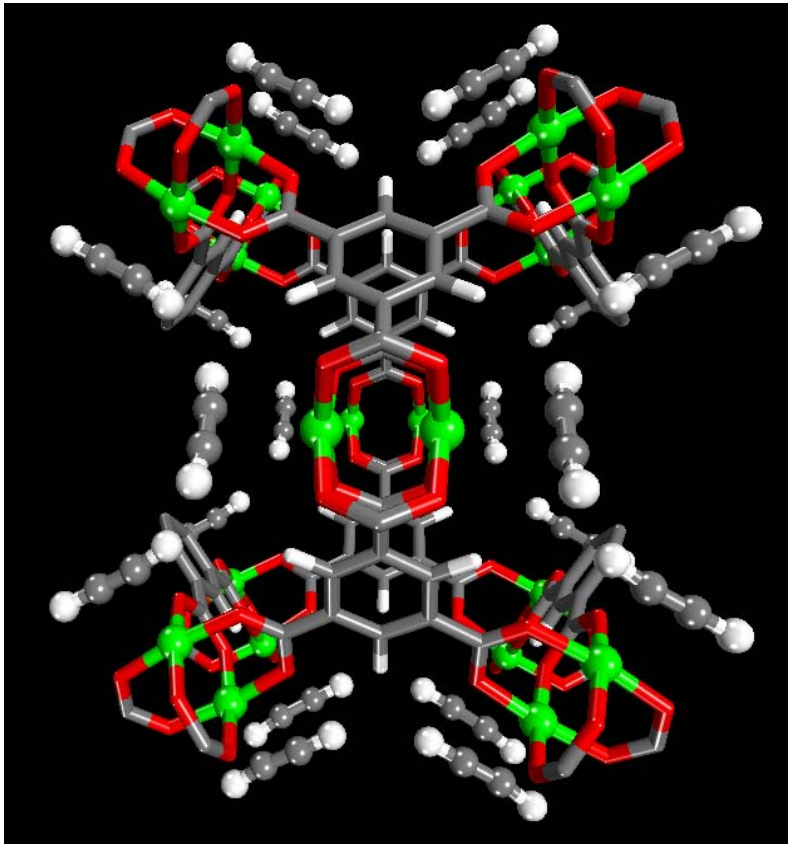


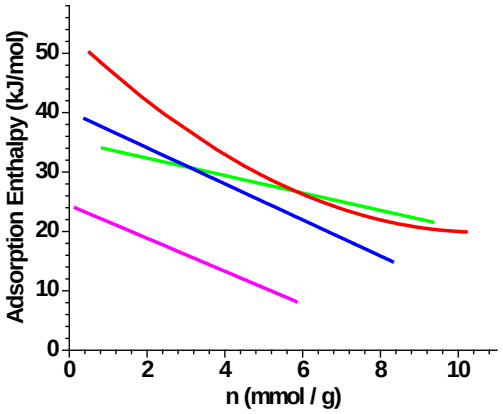
Figure 4 Rietveld refinement of neutron powder diffraction data of 0.62 C_2D_2 per Cu loaded HKUST-1. Crosses, red line, green line, and blue line represent the experimental, calculated, background, difference data points, respectively.

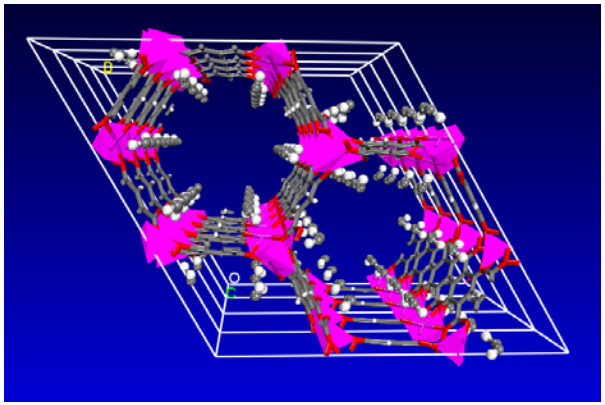
Where are the Acetylene Molecules?

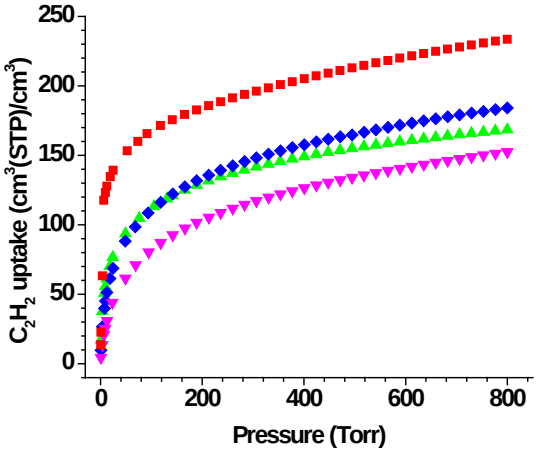


Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc.*, **2009**, *131*, 12415; Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res*, **2010**, *43*, 1115.

Acetylene Storage



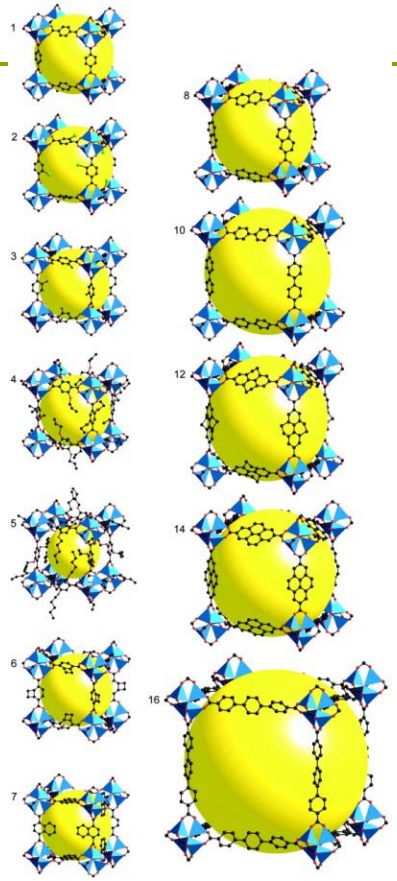


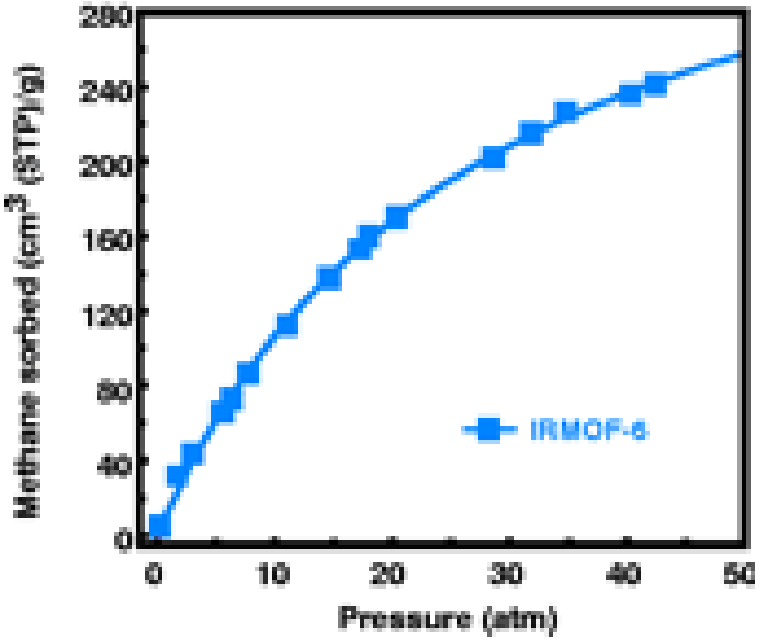


Acetylene adsorption isotherms of microporous MOFs at 295 K (Co_2(DHTP) (red); Mn_2(DHTP) (blue); Mg_2(DHTP) (green); Zn_2(DHTP) (black)).

Xiang, S.; Zhou, W.; Zhang, Z.; Liu, Y.; Chen, B.
Angew. Chem. Int. Ed., **2010**, *49*, 4615.

MOFs for Methane Storage

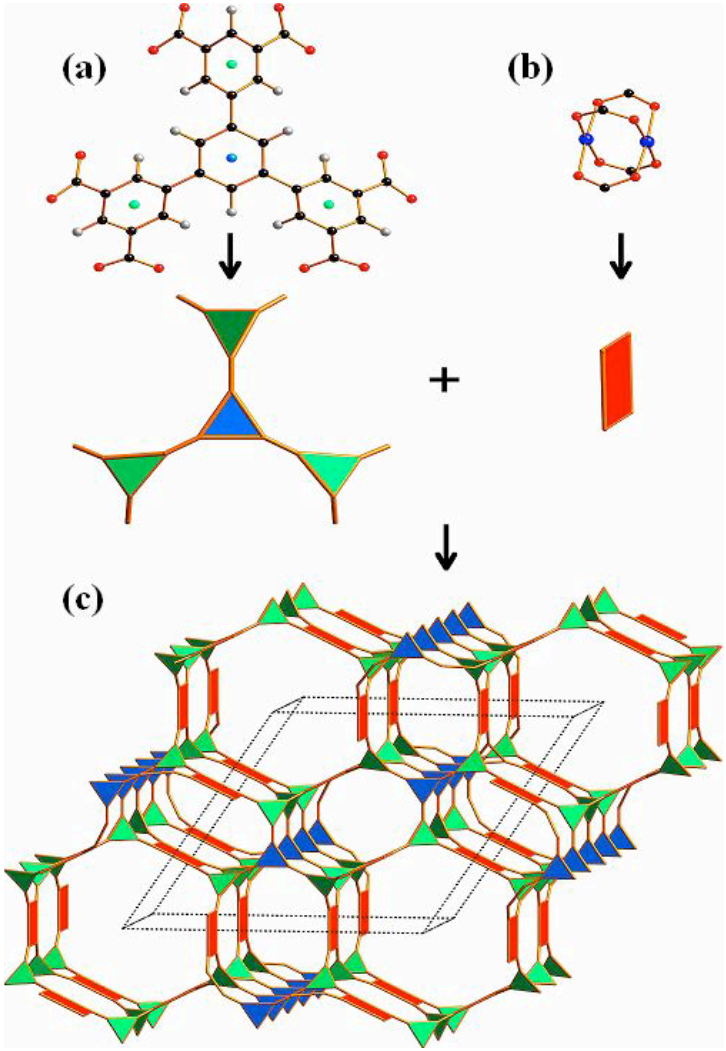




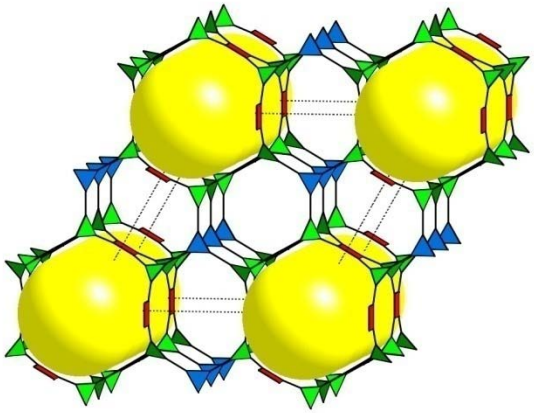
Noro, S.-I., Kitagawa, S., Kondo, M., and Seki, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2081 (146 cm^3/g, 36 atm).

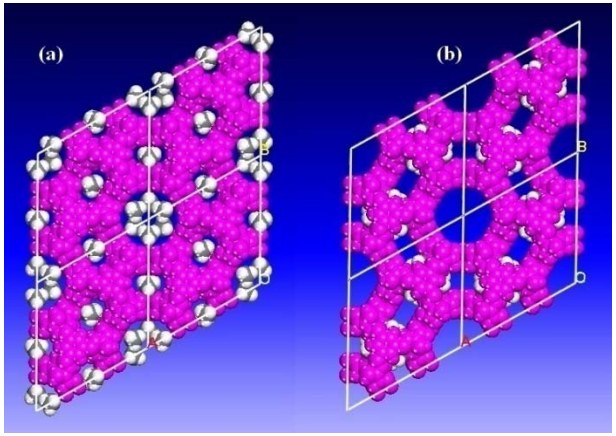
Eddaoudi,, Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., and Yaghi, O. M. *Science*, **2002**, *295*, 469.

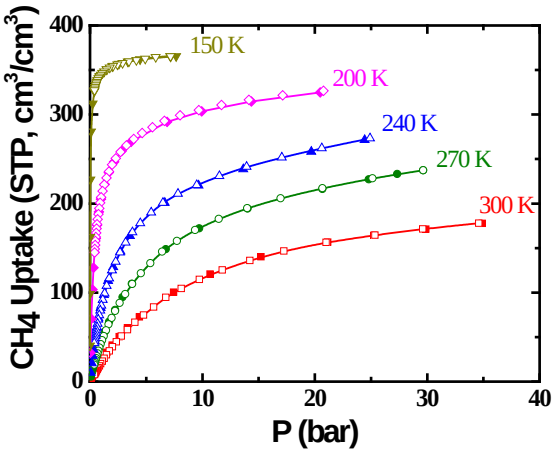
High Density Methane Storage at Room Temperature



High Density Methane Storage at Room Temperature







CH_4 overall uptake of 195 cm^3/cm^3 > DOE standard: 180 cm^3/cm^3

Guo, Z. and Chen, B. et al. *Angew. Chem. Int. Ed.*, **2011**, *50*, 3178.

Conclusions

- Systematic design and synthesis of microporous MOFs for selective sorption of gas molecules.
- The first microporous MOF for GC separation of alkanes.
- Microporous MOF have been developed for large scale separation of gas mixtures by fixed-bed adsorption.
- MOFs with open metal sites for high storage of hydrogen, acetylene and methane.
- M'MOF with the highest hydrogen adsorption enthalpy and their application on C_2H_2/C_2H_4.
- Chiral M'MOF for enantioselective separation.
- Review in *Accounts of Chemical Research*, **2010**, *43*, 1115 (most cited paper).
- Other reviews:

  Chem. Rev. (Luminescent Functional Metal-Organic Frameworks), **2011**, DOI: 10.1021/cr200101d.

  Angew. Chem. Int. Ed. (Functional Mixed-Metal-Organic Frameworks with Metallo-ligands), **2011**, DOI: 10.1002/anie.201101534.

  CrystEngCommun (Microporous Metal-Organic Frameworks for Acetylene Storage and Separation), **2011**, DOI:10.1039/c1ce05437f.
- http://www.sciencewatch.com/dr/sci/misc/Top100Chemists2000-10/

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- Damacio Steven Contreras, Yvette L. Clancy, Fatima Zapata, Eric J. Hurtado, Jose M. Gallegos, Ming Xue, Roxanna M. Schaffino, Shengchang Xiang and Zhangjing Zhang, Zhenxia Chen, Madhab C. Das, Zhiyong Guo
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- NSF, DARPA, DoD, Welch Foundation, National Natural Science Foundation of China and CNMS user program

How promising ?

http://www.youtube.com/watch?v=z-ZRhLapO2s