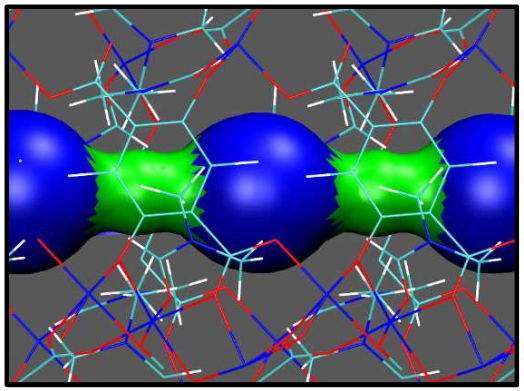
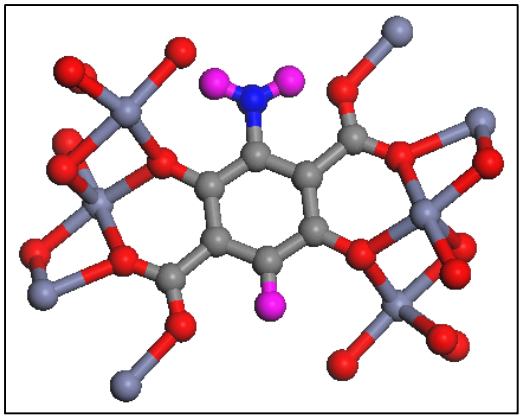
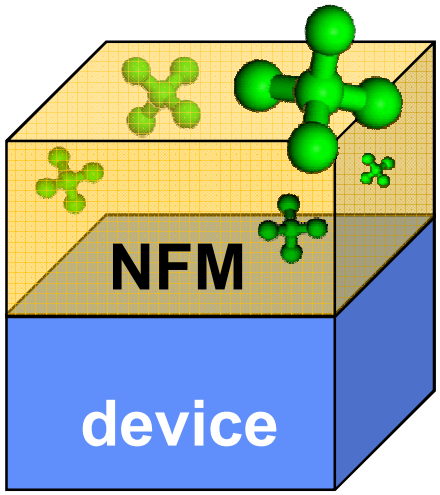
SAND2011-2856C

Computational Modeling of Low-Pressure Gas Detection in Nanoporous Framework Materials







27 April, 2011 4:15 pm

Todd R. Zeitler[1], Mark D. Allendorf[2] and Jeffery A. Greathouse[1]

[1]Sandia National Laboratories, Albuquerque, New Mexico, [2]Sandia National Laboratories, Livermore, California

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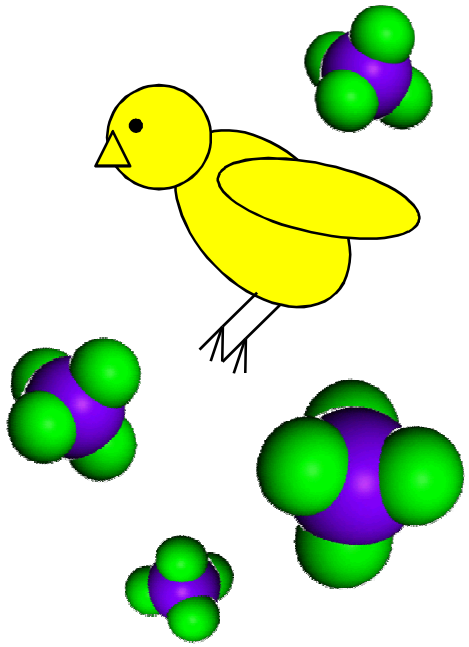
Can NFMs be used to detect methane?

5-15 % CH_4 is explosive

Environmental impact

- **Greenhouse gas accumulation**
- **Landfill leakage**

Main constituent of natural gas

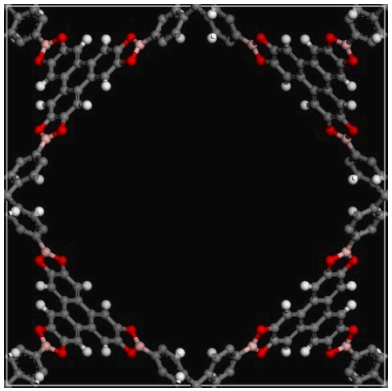


There are 20,000+ NFMs in literature

Which NFMs are good for low-level gas uptake?

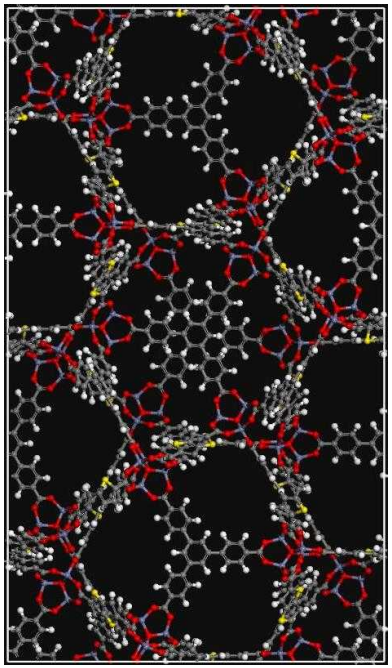
Which NFM properties are useful?

COF-108



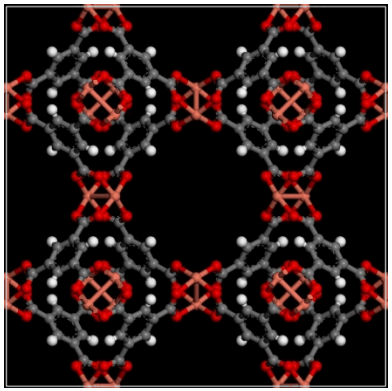
ρ: 0.17 g/cm³

UMCM-2



5000+ m²/g

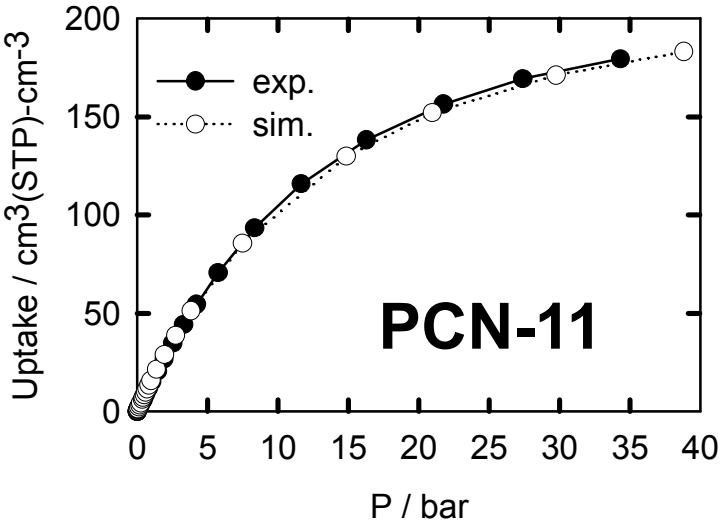
Cu-BTC

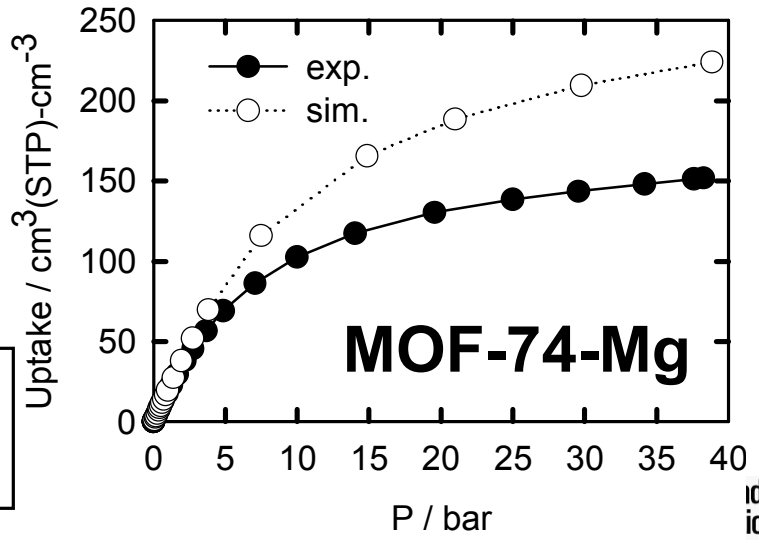


open metal sites / small cages

GCMC simulation is a quick screening tool

- Insertion/deletion
- Loading vs. pressure
- Henry's constant (k_H)
- Initial heat of adsorption (Q_{st})
- Large no. of structures quickly





UFF parameters 298 K

Rigid model of NFM 1-site CH_4 model

Which NFM features enhance low-P uptake?

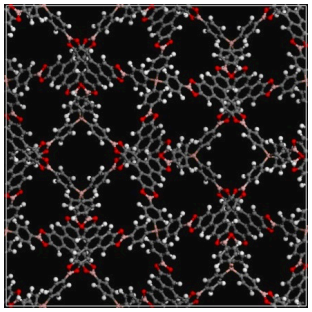
Surface area

Pore diameter

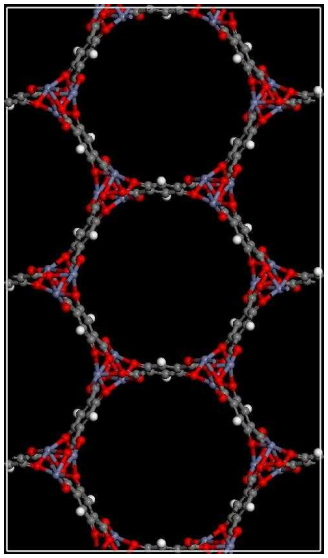
Free volume

Open metal sites

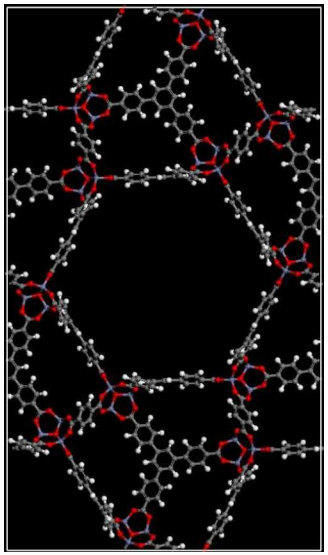
COF



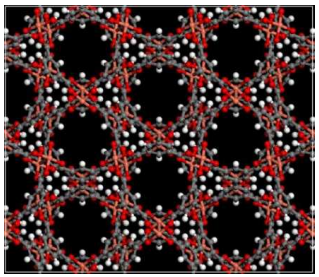
MOF-74-M



UMCM



Cu-based



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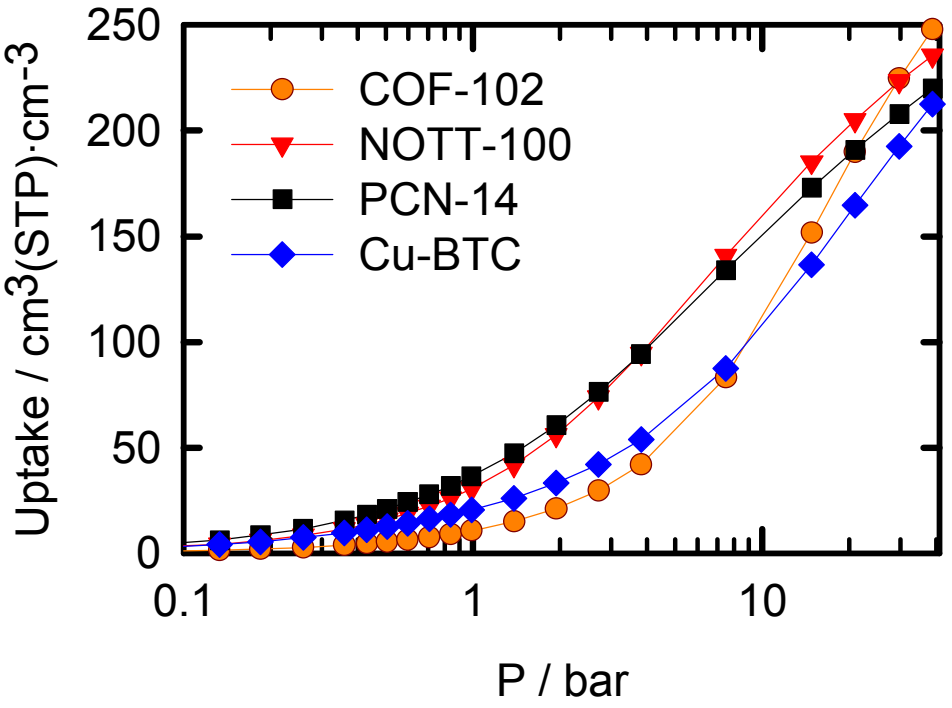
Relative uptake is pressure dependent

NFMs good for high-P CH_4 storage applications not necessarily good at low-P



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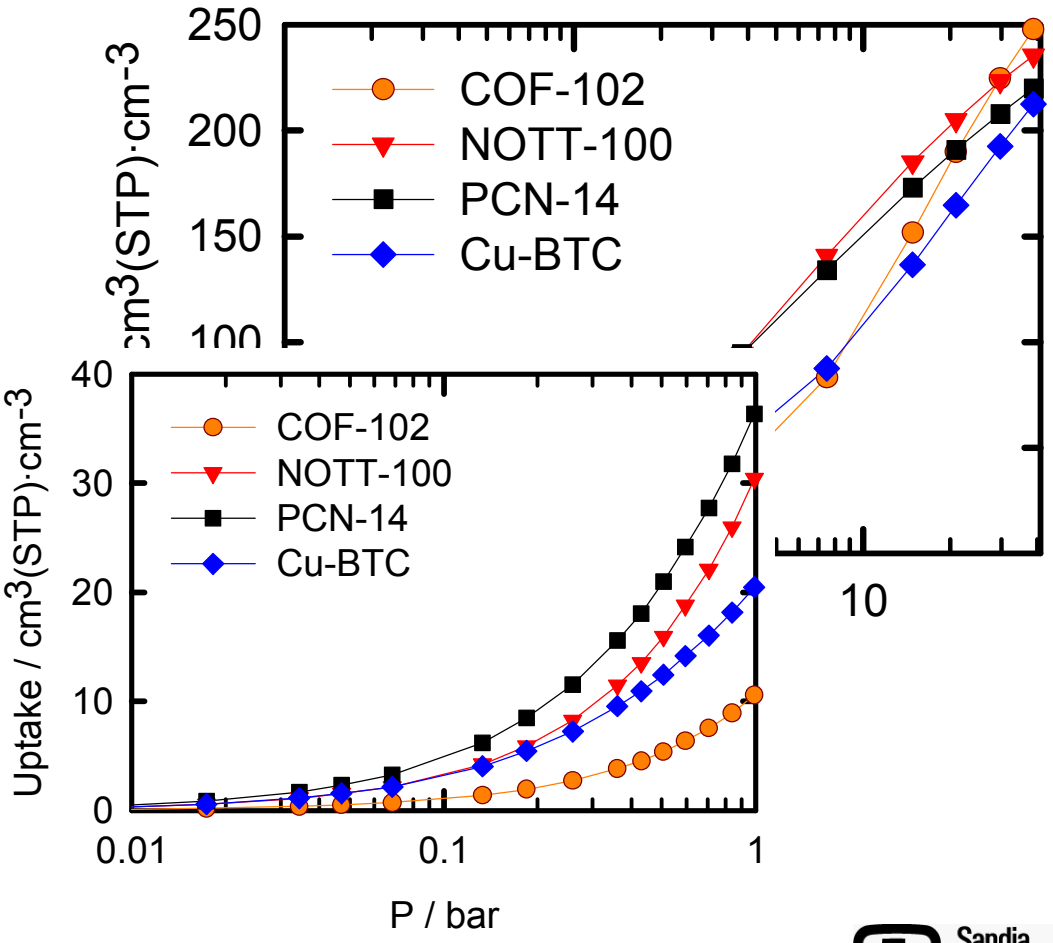

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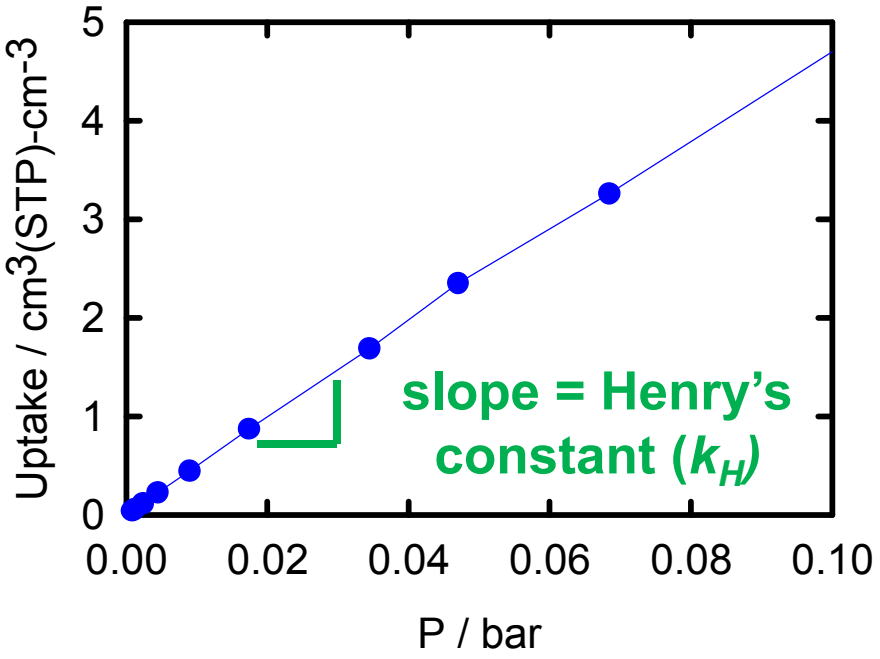
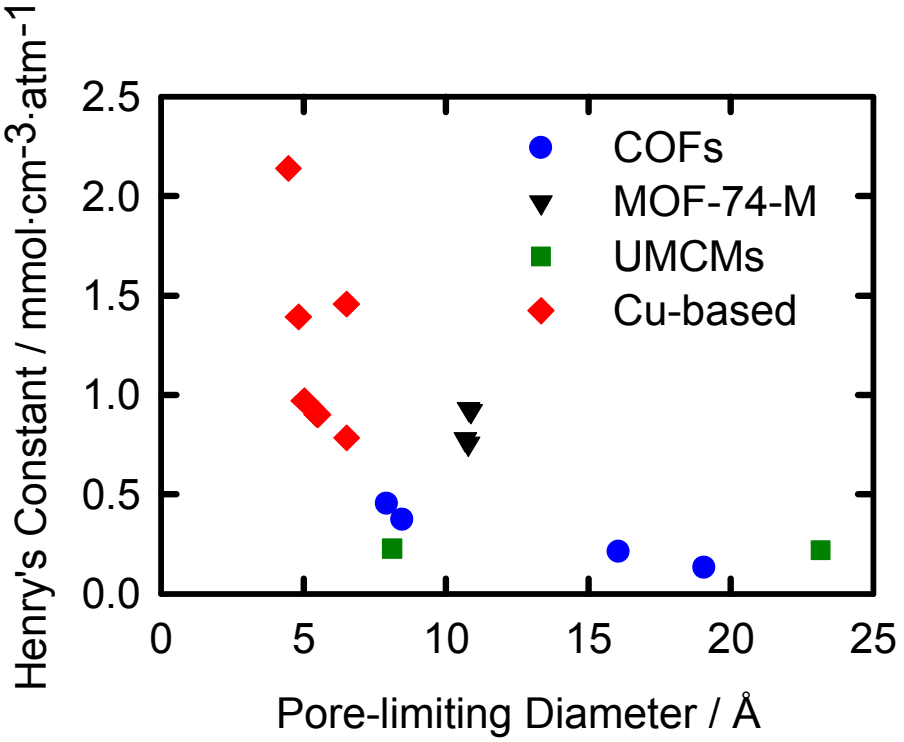
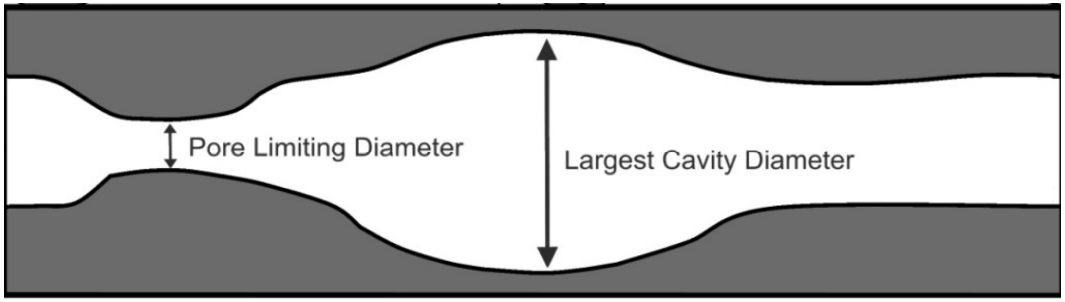
Pore diameter is correlated to initial uptake







Haldoupis, et al. *J. Am. Chem. Soc.* 2010, **132**, 7528-7539.

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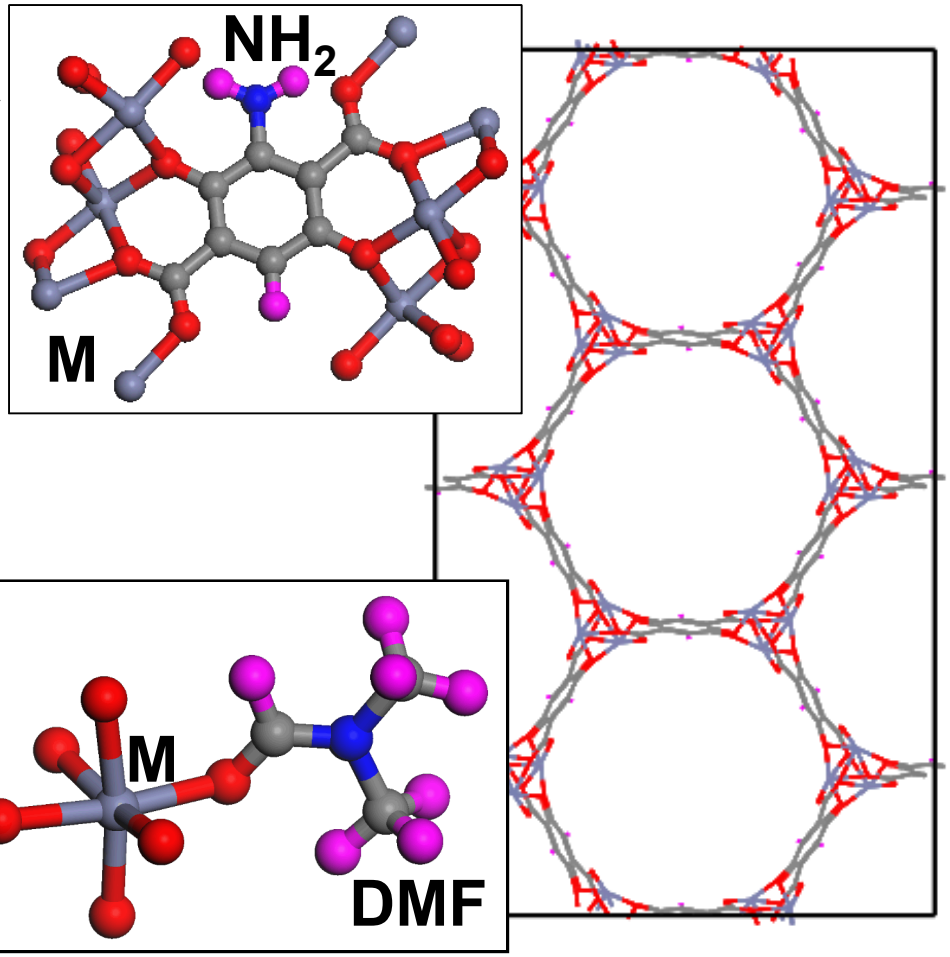
Can functionalization enhance uptake?

Amine (NH_2) on linker

Dimethylformamide (DMF) on metal

MOF-74-M

M = Zn, Ni, Co, Mg



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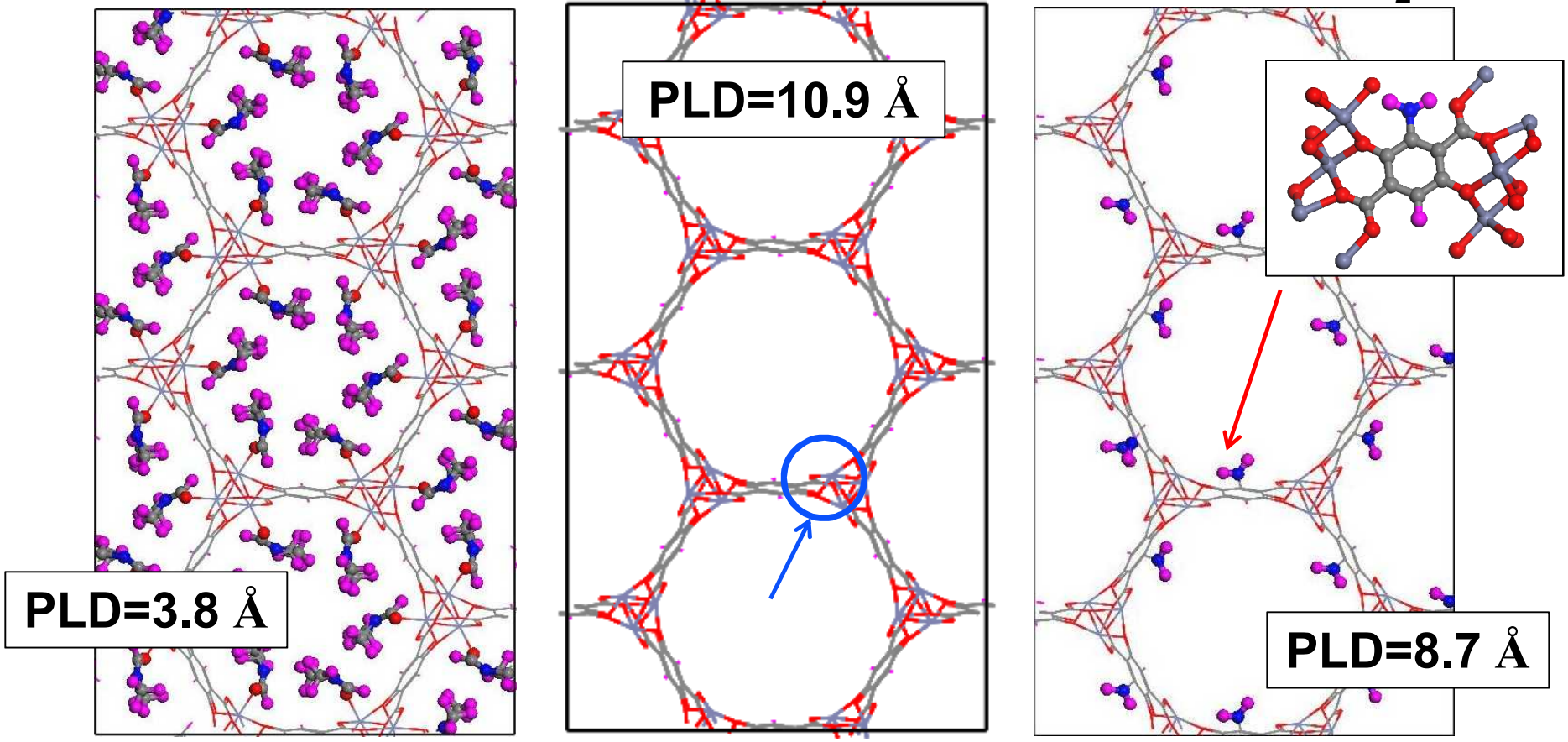
Functionalization changes pore size

MOF-74-Zn-DMF

MOF-74-Zn

MOF-74-Zn-NH_2



MOF w/DMF solvent intact (no open metal sites)

solvent removed (open metal sites exposed)

NH_2 added

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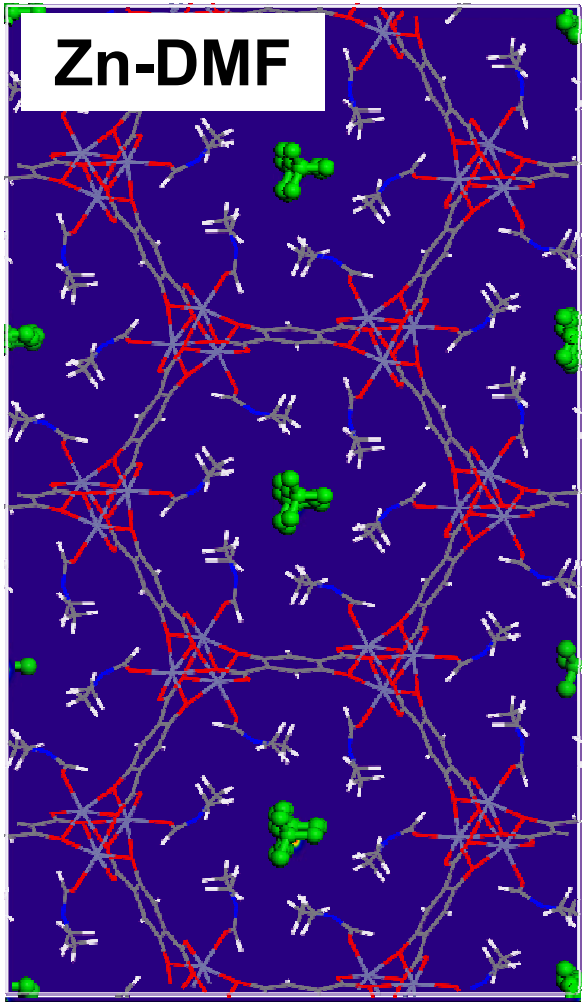
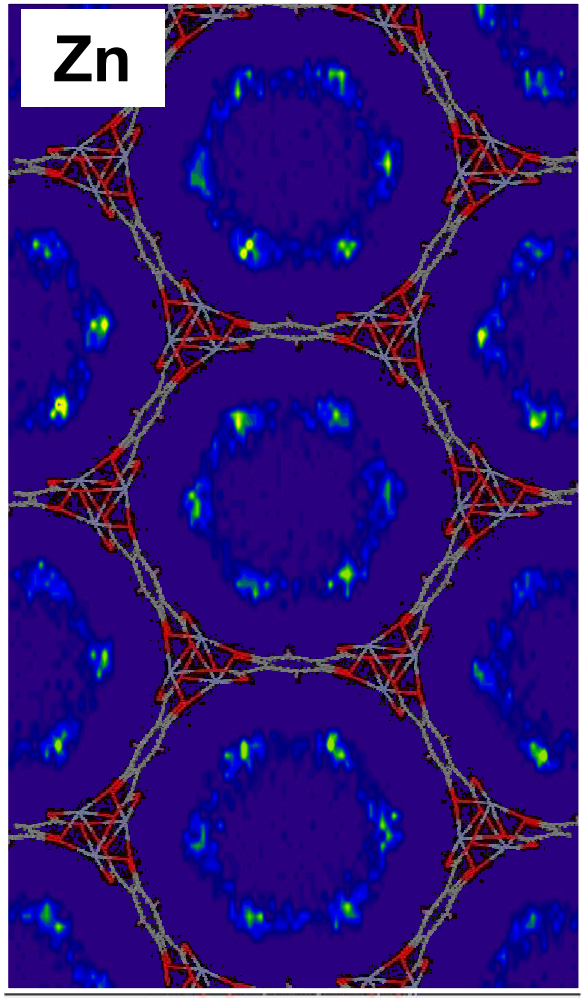
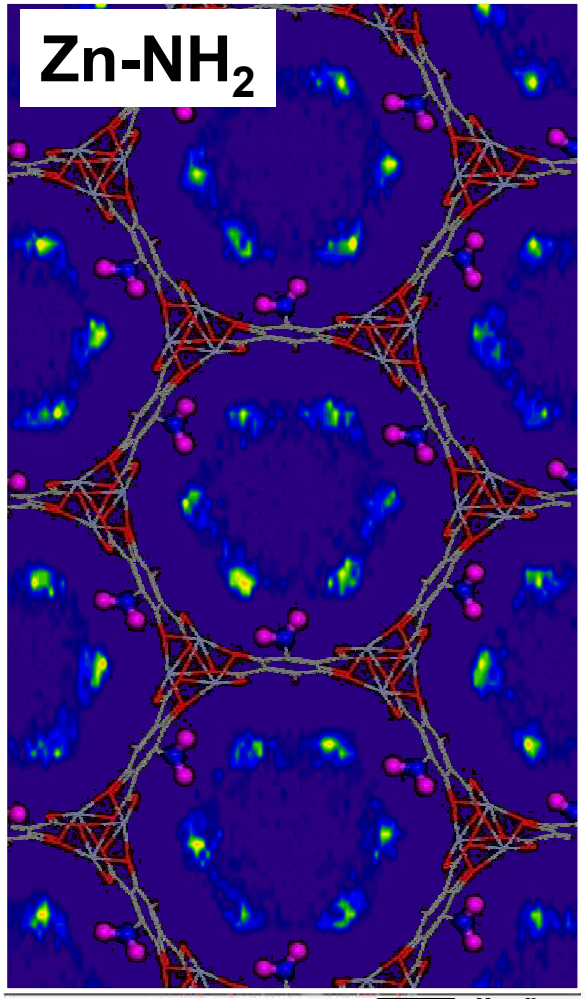
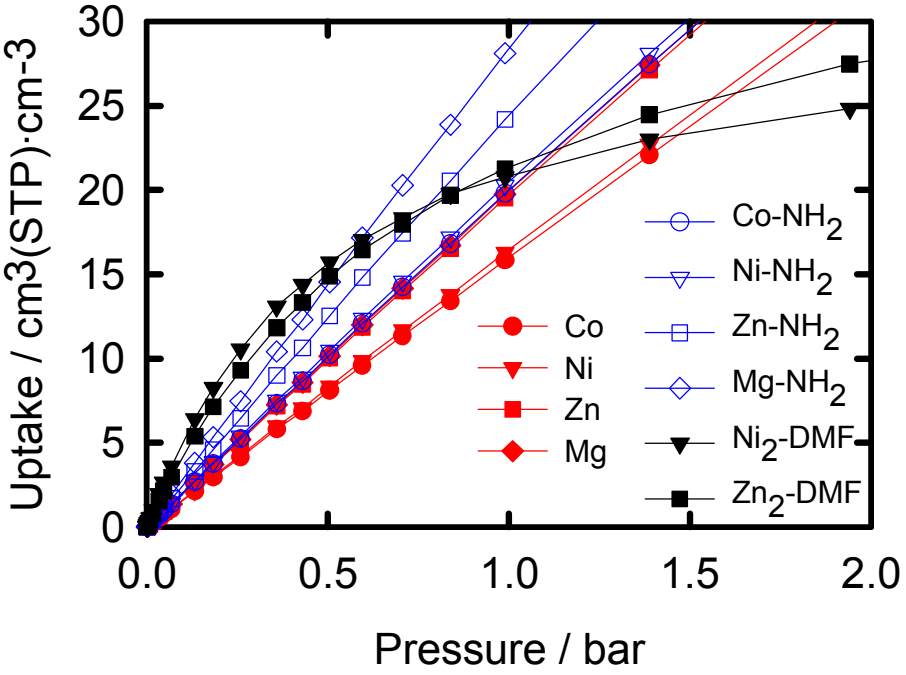
Functionalization influences uptake sites

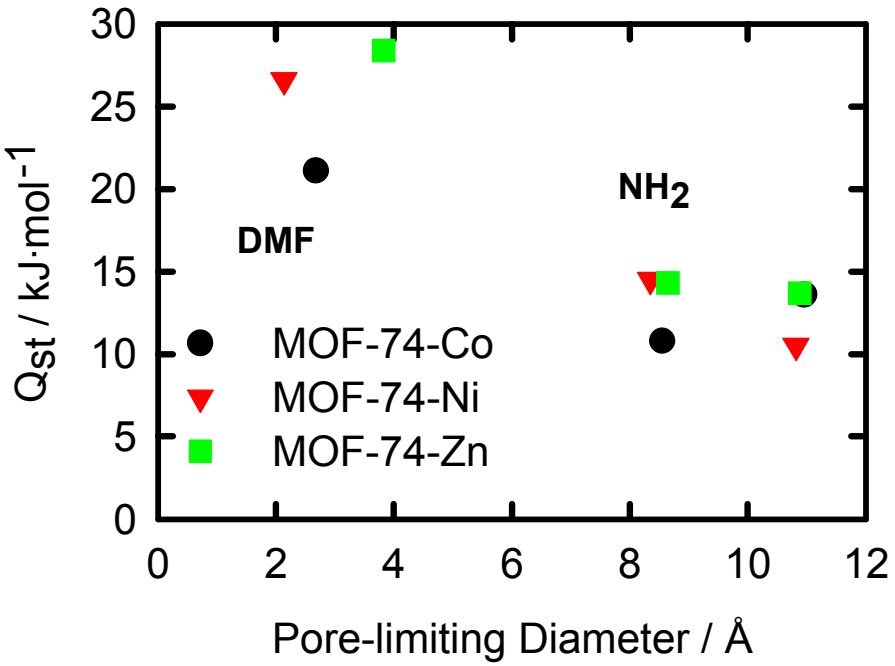






Functionalization enhances low-P uptake





Reduction in pore diameter leads to enhanced uptake.

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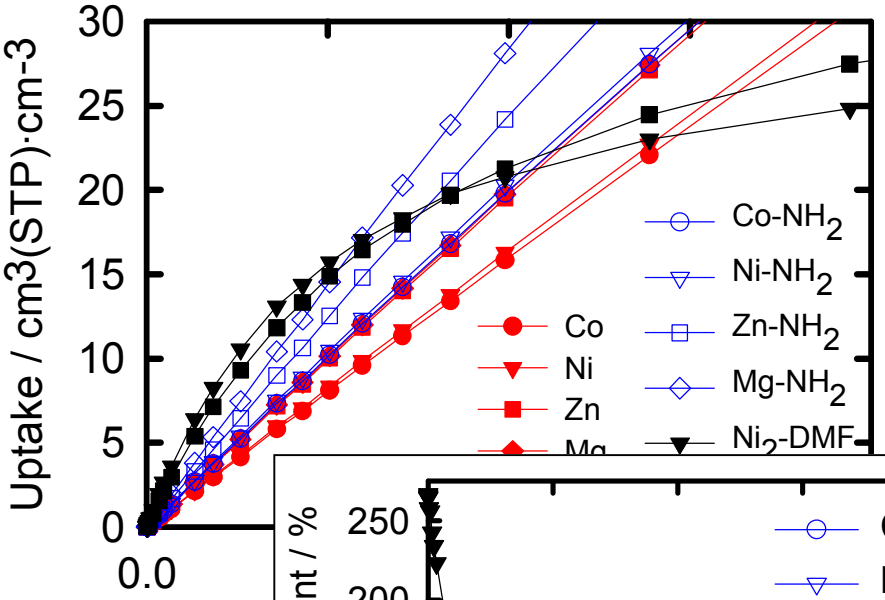
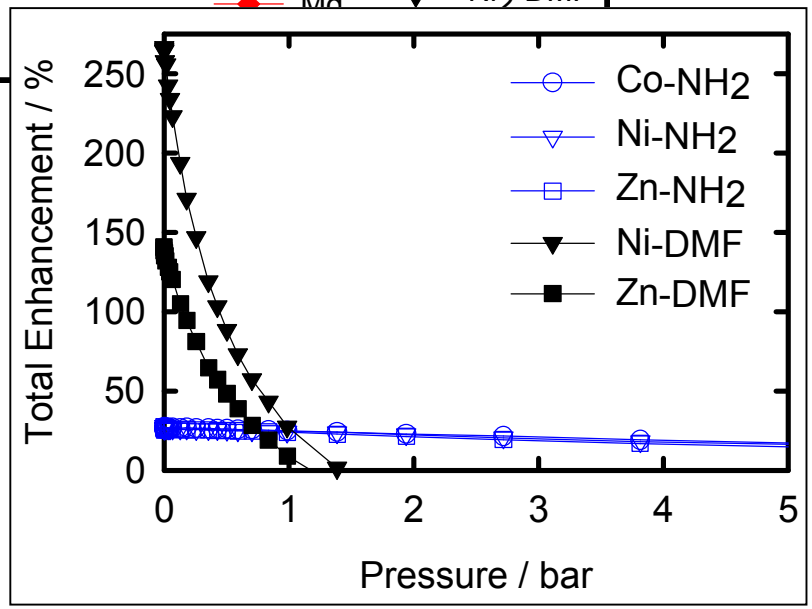
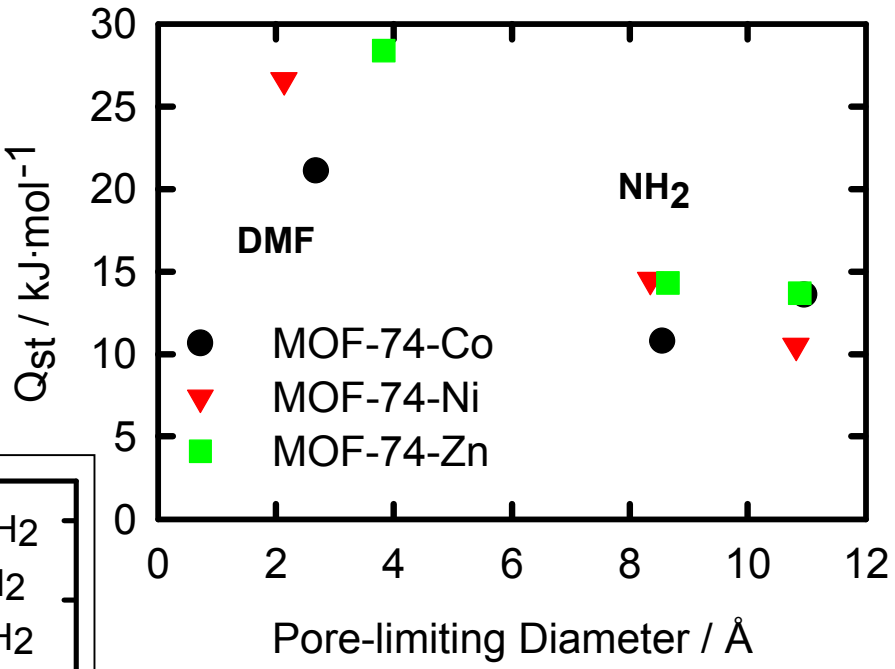
Functionalization enhances low-P uptake







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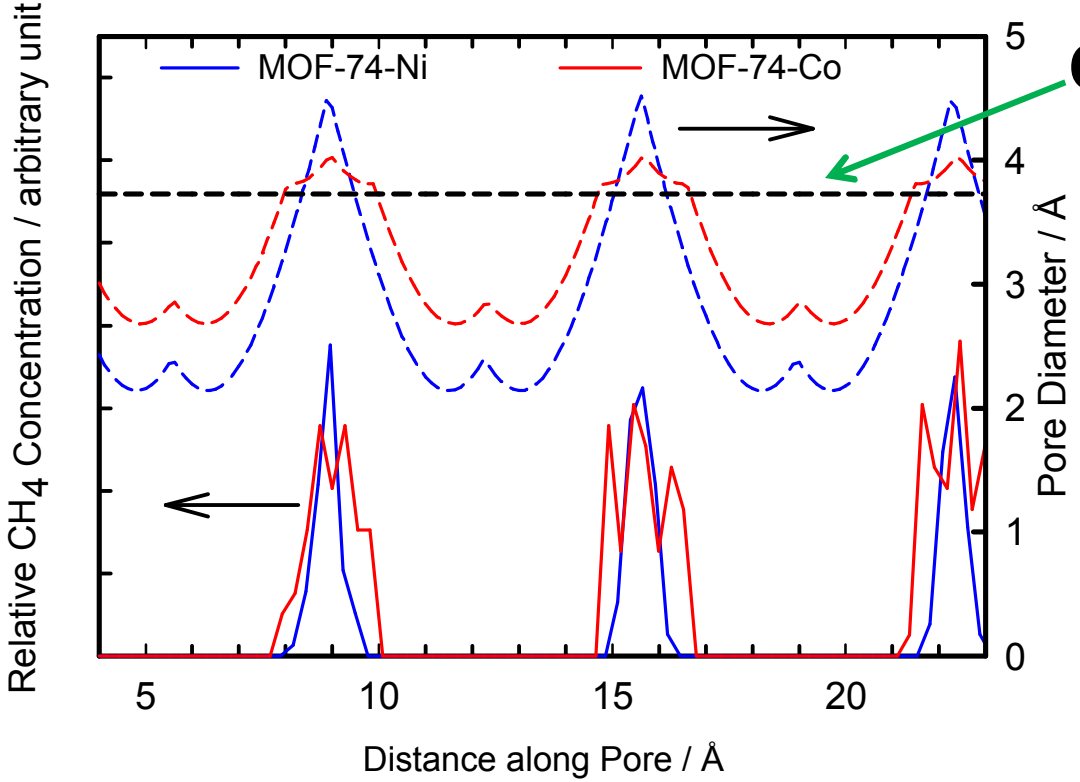
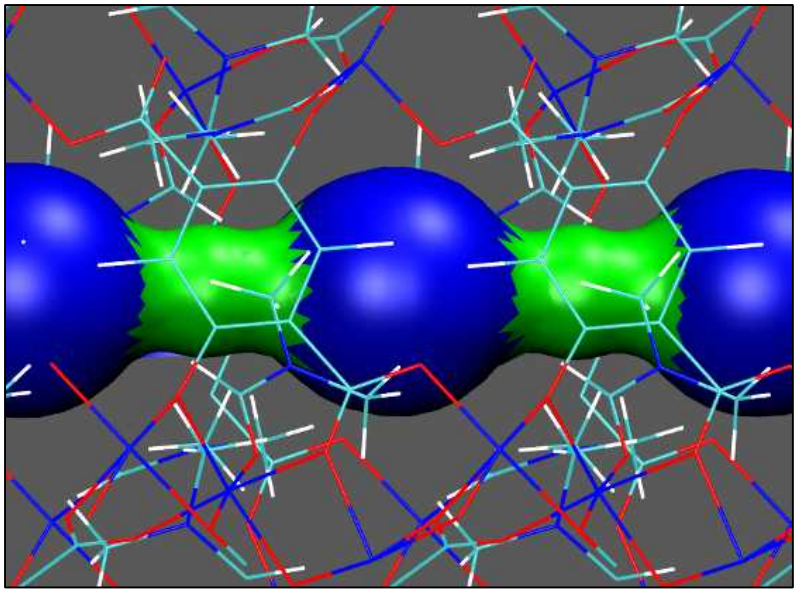
Pore diameter defines adsorption sites



CH_4 diameter



pore mapped along <001>

Adsorption only takes place where pore diameter exceeds CH_4 diameter.

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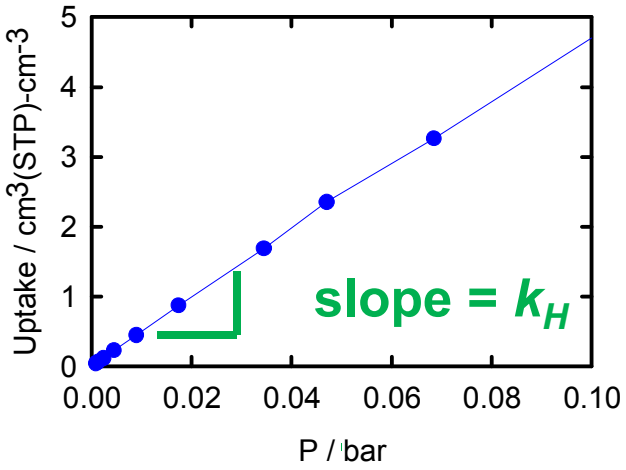
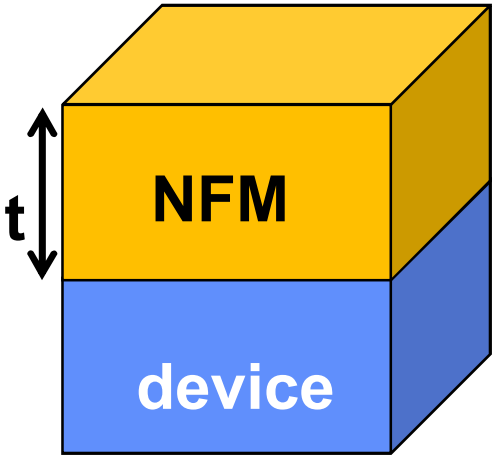
Adsorption results are relevant to detection





$$t = \frac{L_s}{2440 * \rho_{gas,STP} * k_H * P_{gas}}$$

Sensor Type	Sensing Area (cm^2)	Minimum Detectable Mass	Sensing Limit, L_s (ng/cm^2)	Relative Sensitivity
QCM	1.0	1 ng	1.0	1
SAW	0.10	1 pg	0.01	100
MCL	0.00025	1 fg	0.004	250

- ***t:*** **minimum NFM thickness (nm)**
- **L_s: sensing limit (ng/cm^2)**
- **$\rho_{gas,STP}$: gas density @ STP (g/cm^3)**
- **k_H: Henry's constant (v(STP)/v·bar)**
- **P_{gas}: partial pressure of analyte (bar)**

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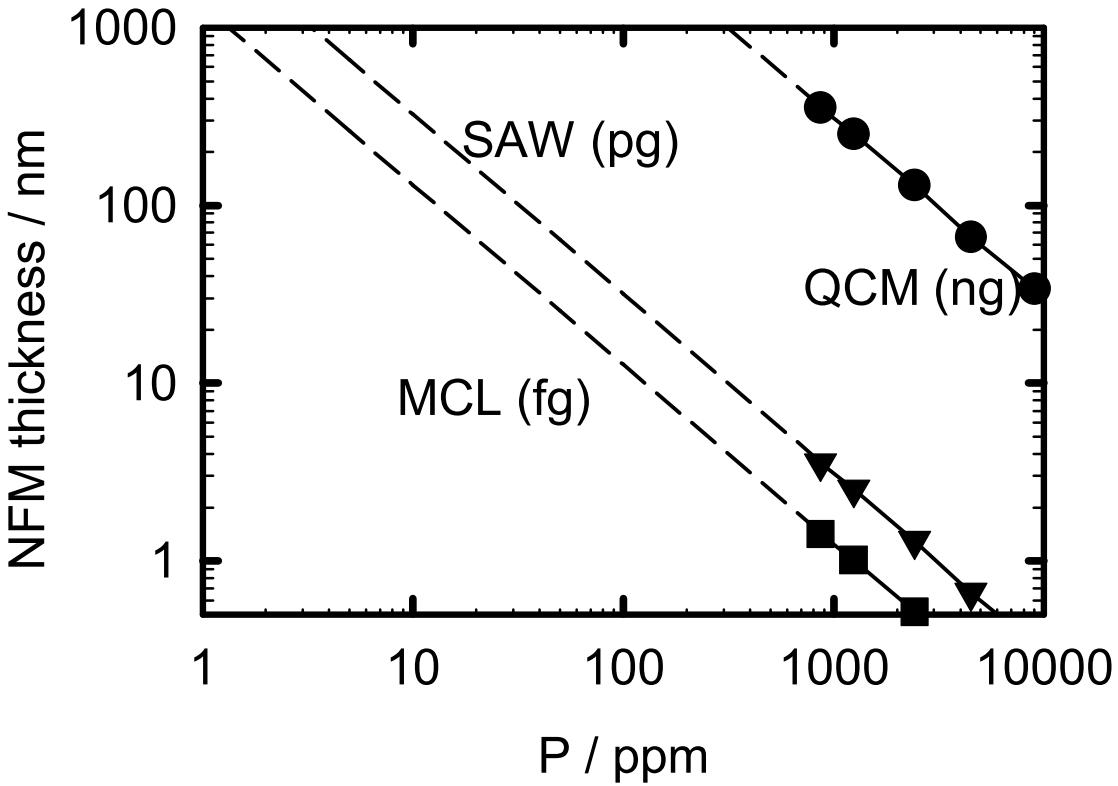
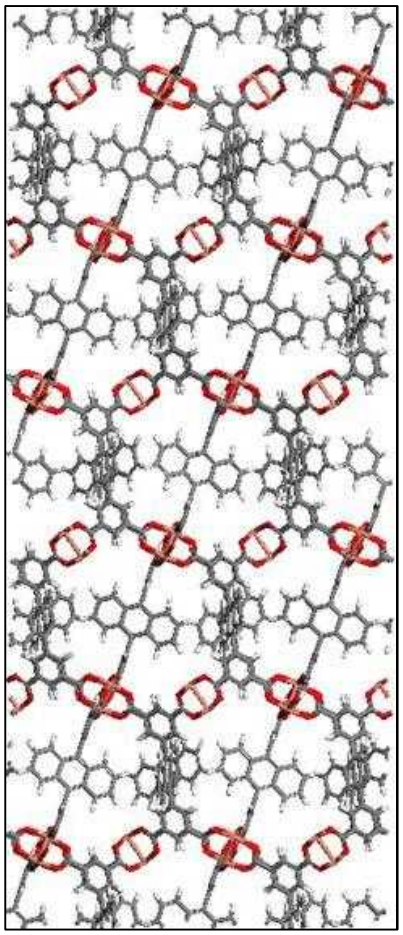
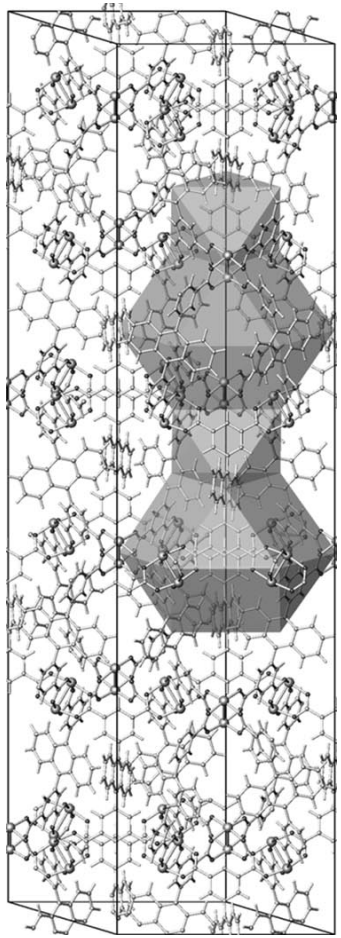
Minimum NFM thickness for detection limit







PCN-14 has highest k_H of NFMs in this study

Wu, et al. Chem.-Eur. J. 2010, **16**, 5205-5214.

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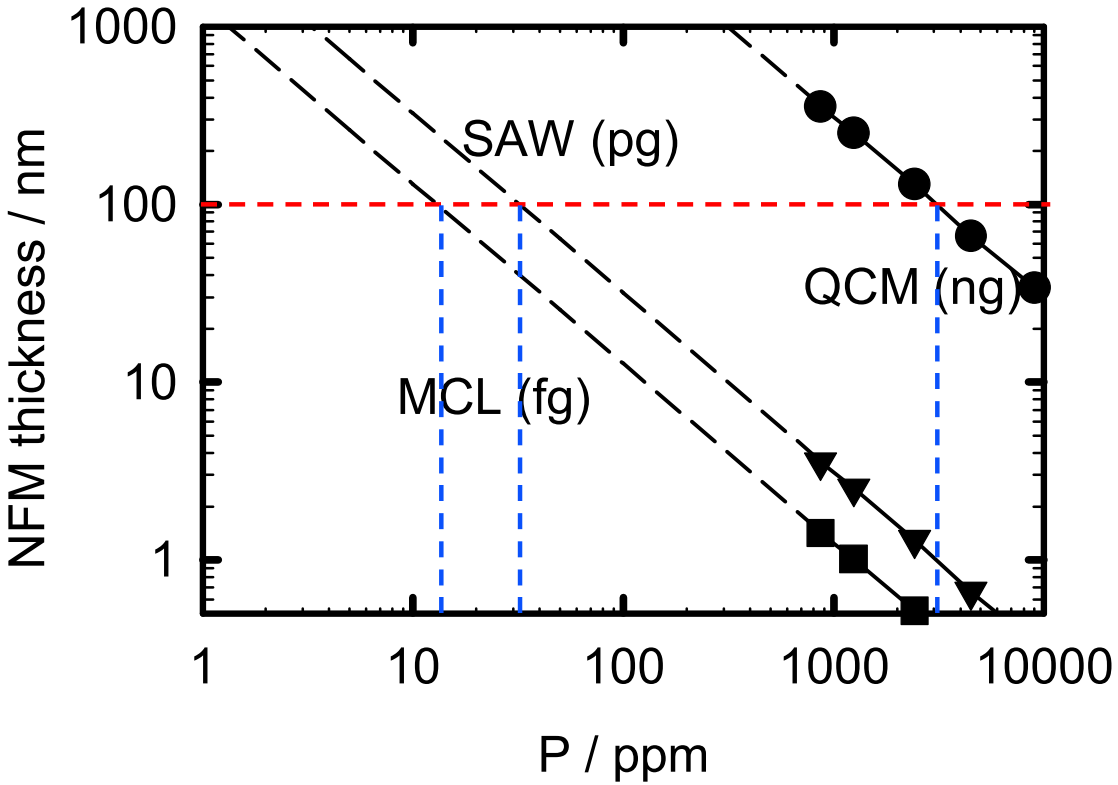

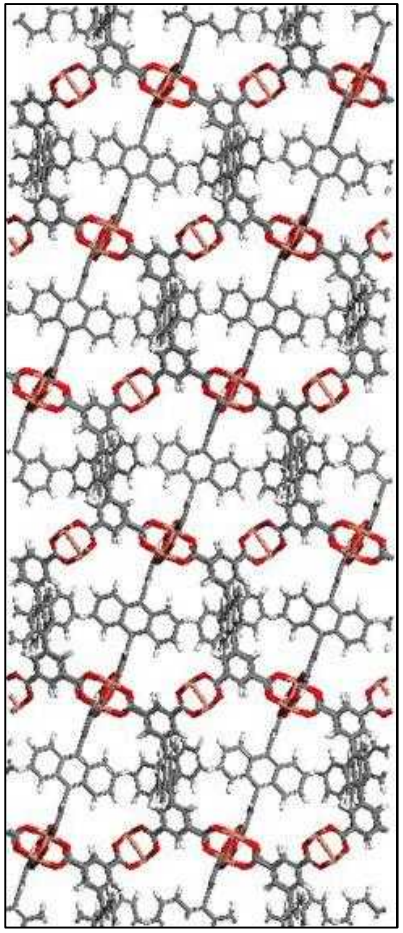

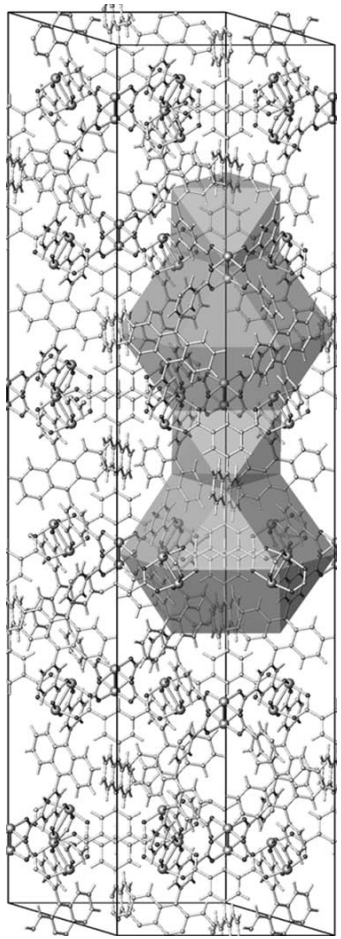

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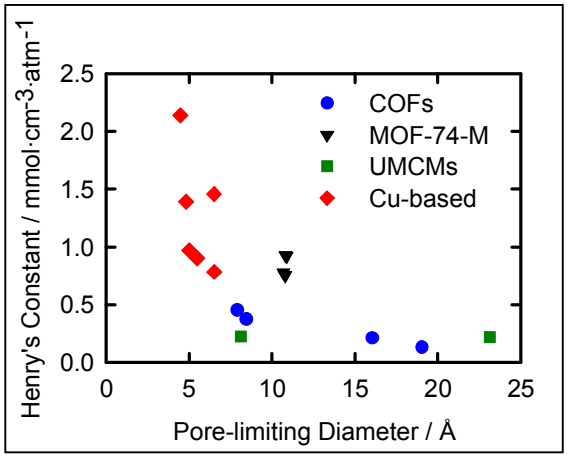
Conclusions

NFMs for low-level CH_4 uptake should have small pores.

- **PLD ~ diameter of CH_4 molecule**

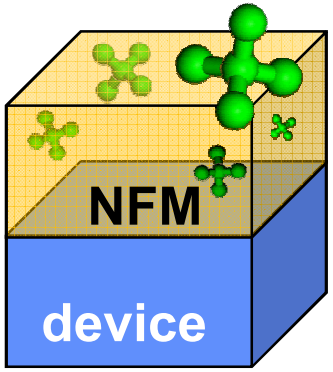


Functionalization can enhance uptake.

- **Linker—NH_2 ~ 25 %**
- **Pore solvent—DMF 100-250 %**

Hypothetical minimum NFM layer thickness for sensing devices

$$t = \frac{L_s}{2440 * \rho_{gas,STP} * k_H * P_{gas}}$$



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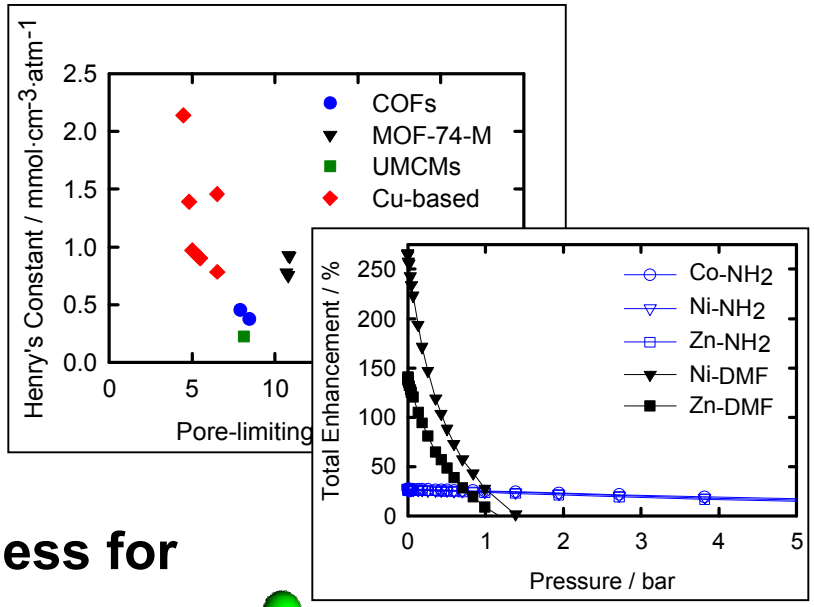

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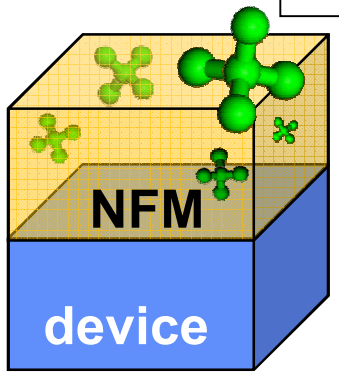

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