Stimuli-Responsive Metal-Organic Frameworks for Energy-Efficient Post-Combustion CO_2 Capture

Hong-Cai (Joe) Zhou, Hae-Kwon Jeong, and Perla B. Balbuena, Texas A&M University

DE-AR0000073

PROJECT GOAL

The goal of this work is to develop **innovative metal-organic framework-based molecular sieves whose adsorption and desorption properties can be finely tuned for energy-efficient post-combustion CO_2 capture from coal-fired power plants**

MOTIVATION

- Coal-fired power plants are the single largest anthropogenic CO_2 emission sources domestically and globally
- Post-combustion CO_2 capture can be retrofitted to existing plants (in contrast to oxy-combustion or pre-combustion capture technologies)
- DOE/NETL goal : 90% CO_2 capture at less than 35% increase in the cost of electricity
- Finding novel sorbents for commercialization by partner, **framergy™** (www.framergy.com) is paramount to this goal

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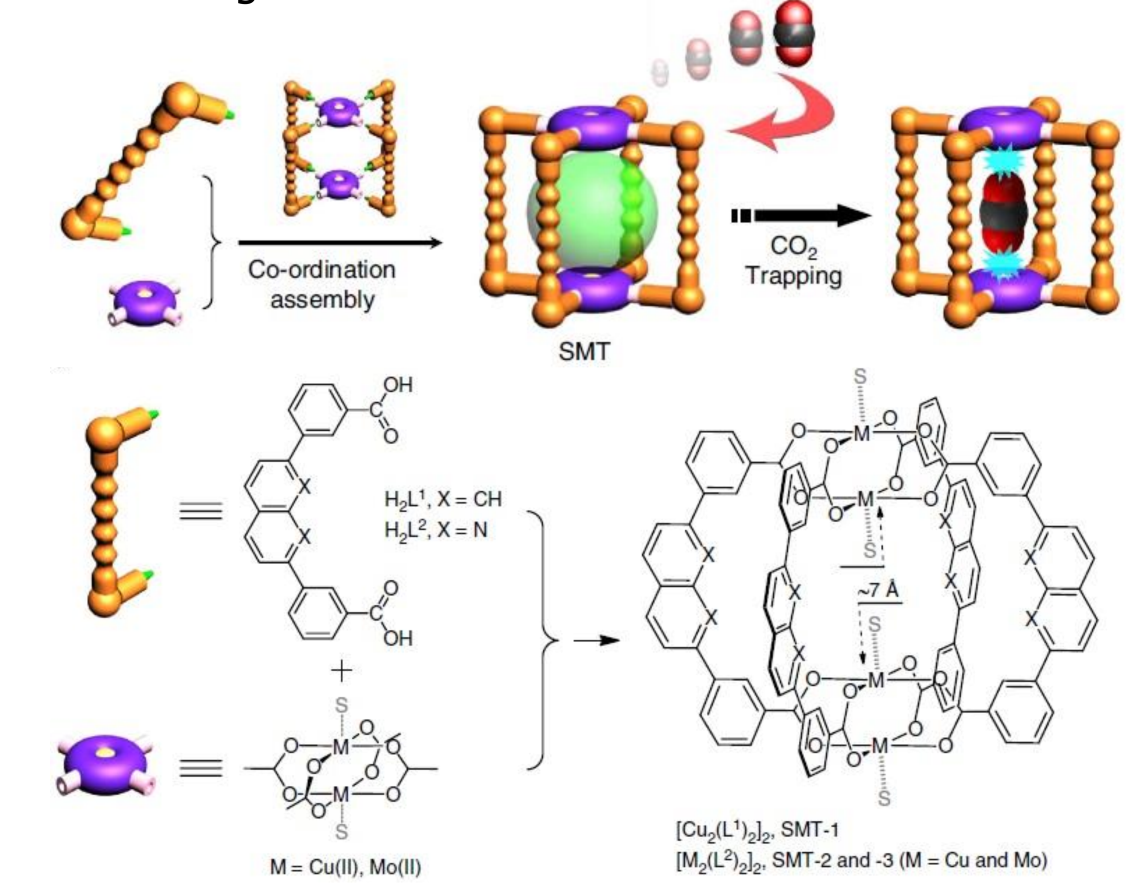
Why Stimuli-responsive Metal-Organic Frameworks?

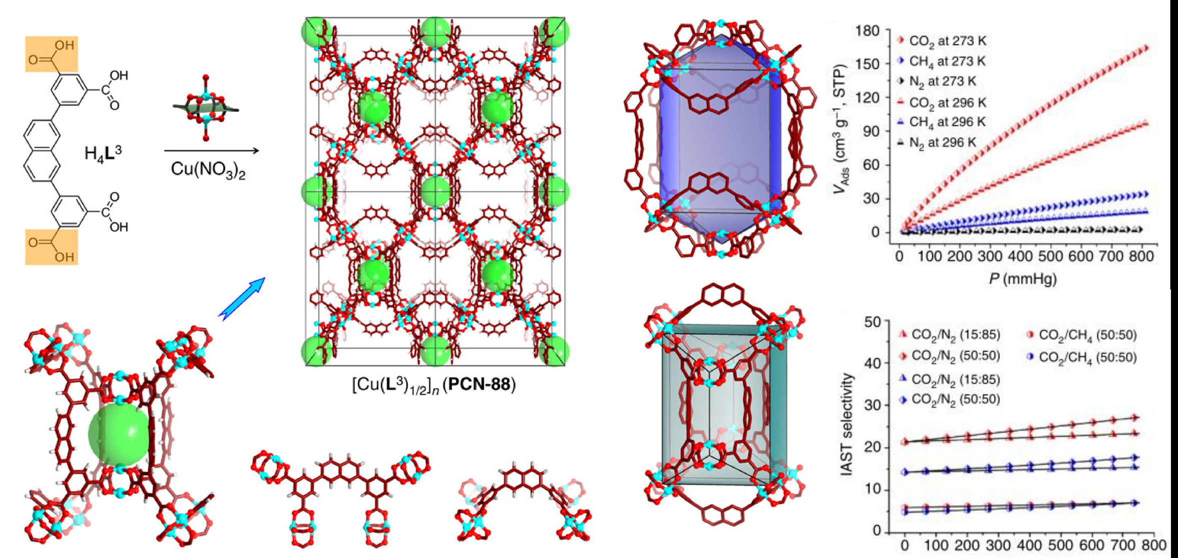
- **Metal-Organic Frameworks:** physisorbents with high surface area, tunable pore size, and physico-chemical functionalities
- **High CO_2 / N_2 selectivity**: sorption properties can be tuned specifically for CO_2 (i.e. adjusting the size of its mesh by slightly changing temperature)
- **High CO_2 loading:** MOF materials are highly porous materials with high surface area, thereby exhibiting high CO_2 loading. Tuning the length of organic ligands can control the pore/cavity size thereby the CO_2 uptake
- **Efficient regeneration:** slight increase in temperature (e.g. ΔT regeneration ~ 10°C) will release CO_2 by opening up the gates

Single molecular traps (SMTs)

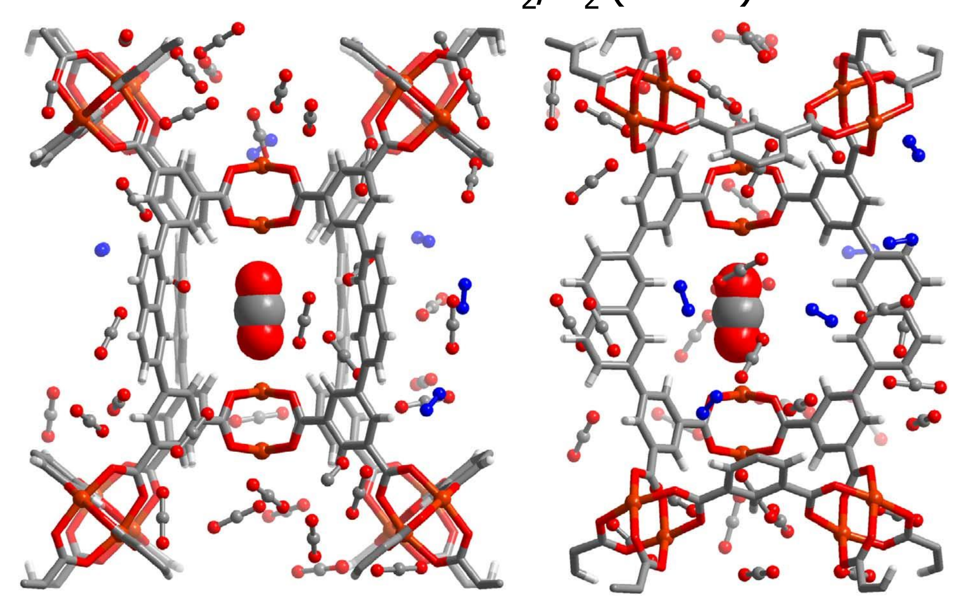
1. SMT design and construction



2. MOF with built-in SMTs



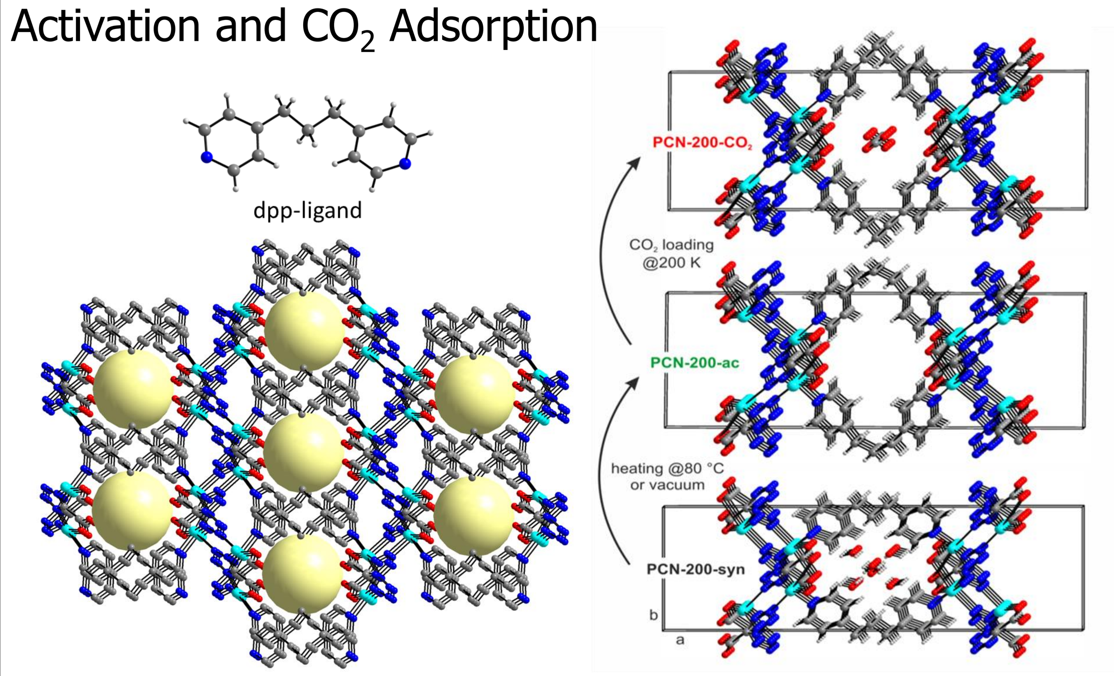
3. Simulated locations for CO_2/N_2 (15:85) mixture



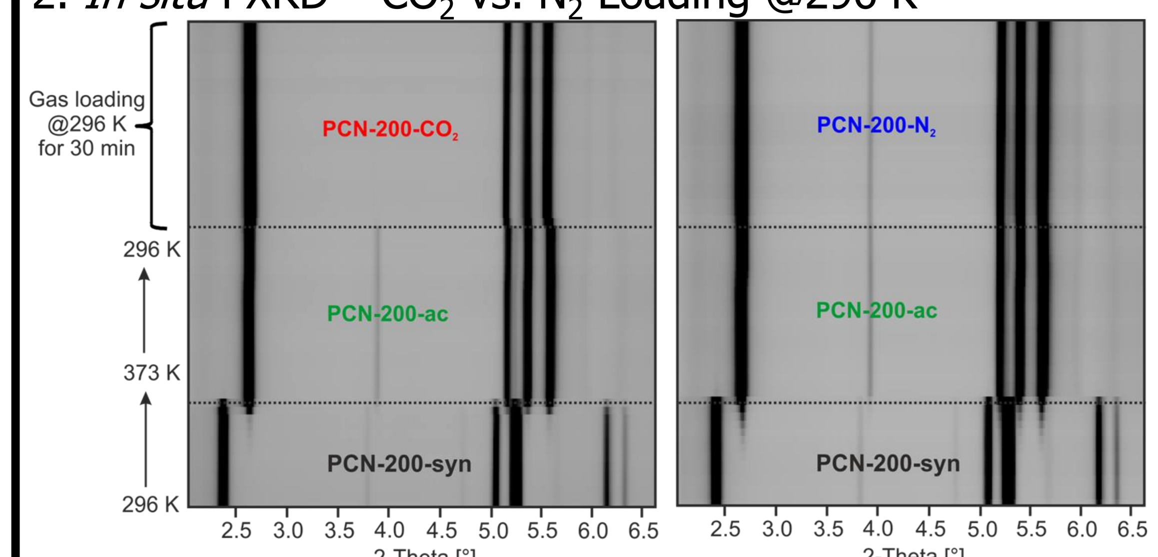
Ref.: *Nature Commun.* 2013, DOI: 10.1038/ncomms2552.

Stimuli-responsive MOF

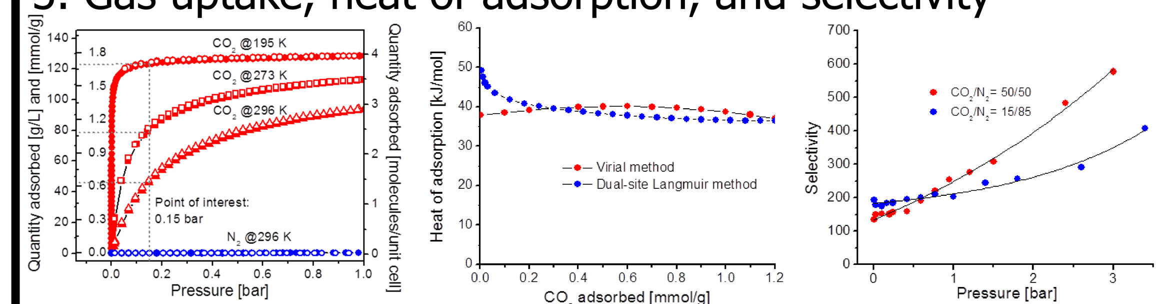
1. MOF structure and Structural Changes upon Activation and CO_2 Adsorption



2. *In situ* PXRD – CO_2 vs. N_2 Loading @296 K



3. Gas uptake, heat of adsorption, and selectivity

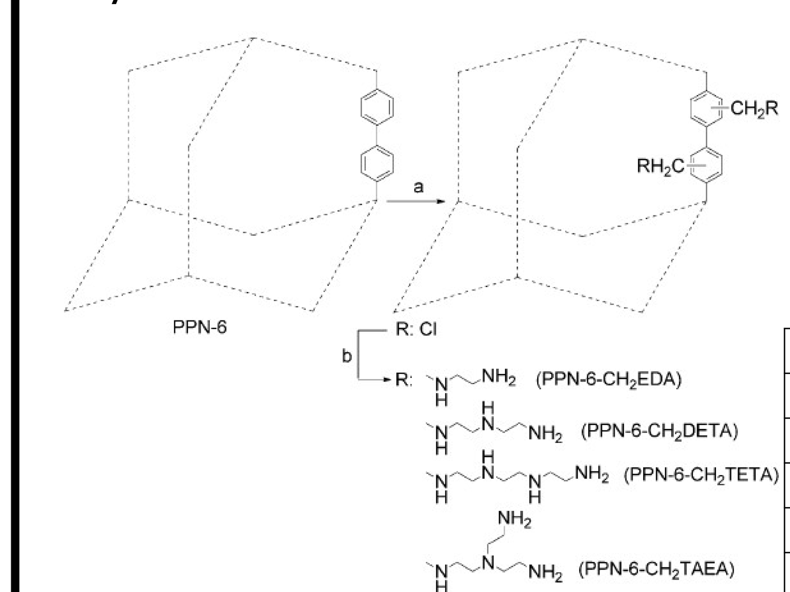


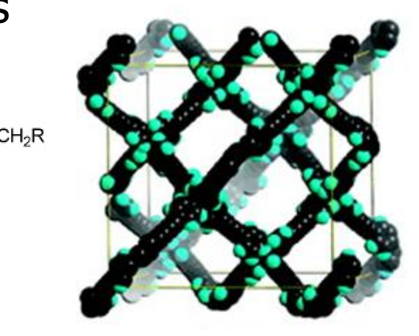
- 3D MOF with 1D channels
- High selectivity for CO_2 over N_2 (>200)
- High heat of adsorption for CO_2
- Easy scale up
- $4.10/g
- Air, SO_x/NO_x, and water stable
- Chemical (pH 2-12) stable
- Thermal (up to 220 °C) stable
- low regeneration cost

Ref.: *Angew. Chem. Int. Ed.* 2012, 51, 9804–9808.

Amine-Tethered PPNs

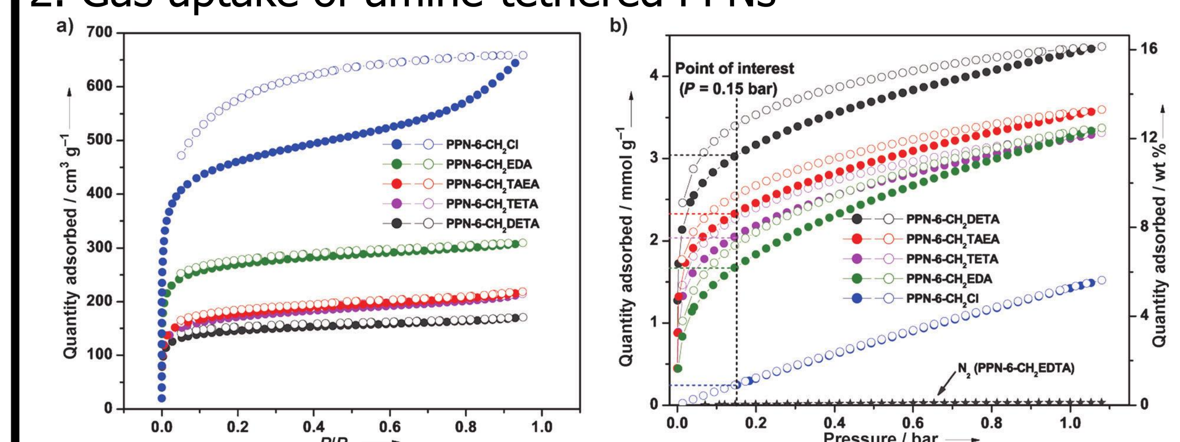
1. Synthesis of amine-tethered PPNs



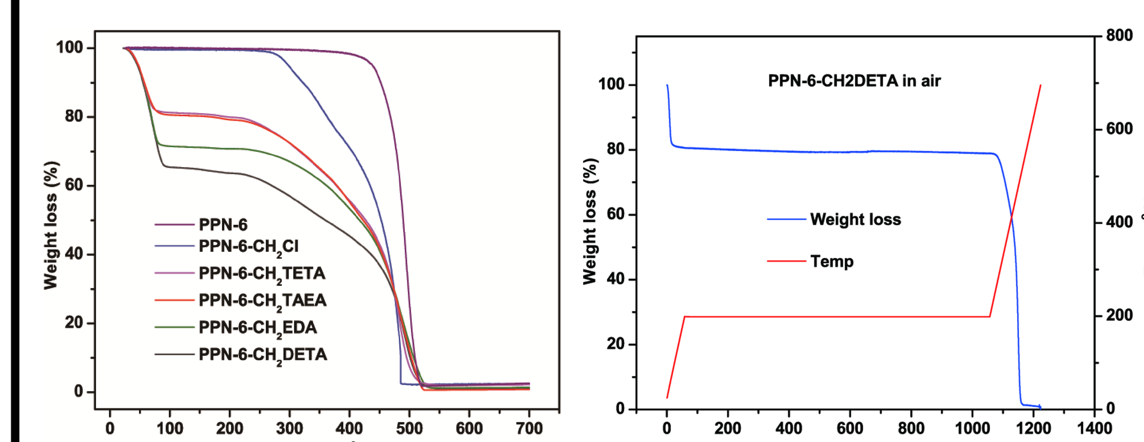


	Cl%	N%
PPN-6-CH2Cl	14.42	0.0
PPN-6-CH2EDA	0.33	7.53
PPN-6-CH2TAEA	< 0.25	9.31
PPN-6-CH2TETA	< 0.25	9.04
PPN-6-CH2DETA	< 0.25	11.95

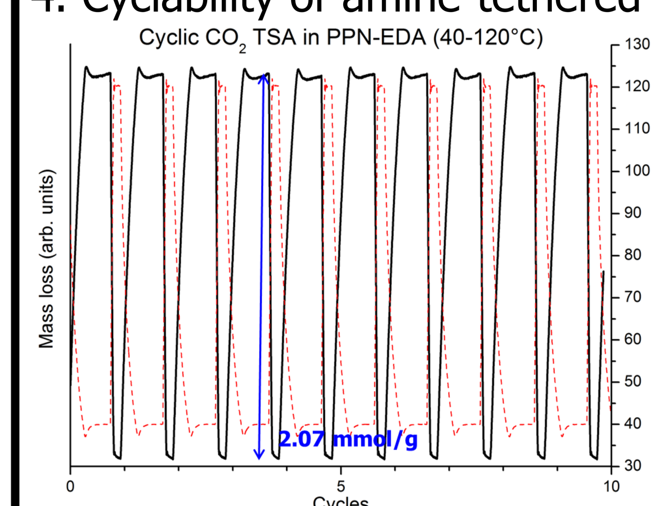
2. Gas uptake of amine-tethered PPNs



3. TGA of amine-tethered PPNs in air



4. Cyclability of amine-tethered PPNs



- Covalent bonds
- High surface area
- High uptake
- Low density
- High thermal Stability
- High chemical stability

Ref.: *Angew. Chem. Int. Ed.* 2012, 51, 7480–7484.

Summaries

- Innovative stimuli-responsive MOFs have a great potential for efficient post-combustion CO_2 capture
- A new concept, the 'SMT' has been utilized in designing porous materials at the molecular level for CO_2 adsorption applications
- PCN-200 is very promising with high CO_2/N_2 selectivity, low cost, high chemical (SO_x/NO_x)/thermal stability, easy regeneration
- Amine-tethered PPNs show comparable CO_2 working capacity to MEA with much lower energy consumption

CHEMISTRY TEXAS A&M UNIVERSITY

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