Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling

DE-FE0031960

Thien (James) Tran

University at Buffalo, The State University of New York

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021

Program Overview

a. Funding (DOE: \$800,000; Cost Share: \$206,330)

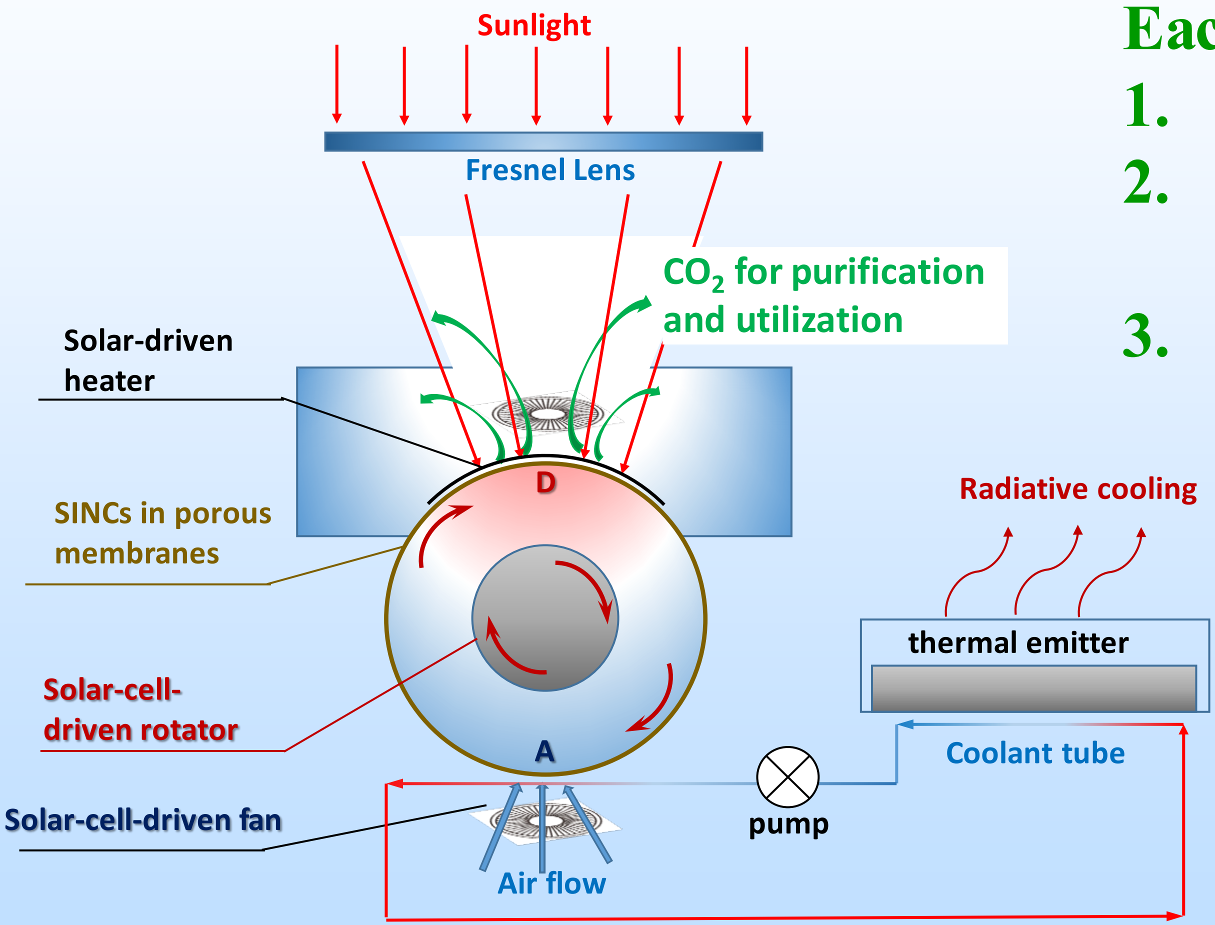
b. Overall Project Performance Dates: 10/1/20 – 3/31/22

c. Project Participants: University at Buffalo (UB) and Trimeric Corporation (Trimeric)

d. Overall Project Objectives

- Year 1: design and prepare membrane adsorbent based on CO_2-philic polymers and SINCs, and design operation cycles with solar heating and radiative cooling for CO_2 capture from air.
- M13-M18: construct and characterize a DAC prototype, demonstrate the 100-h continuous operation for DAC, and complete the TEA.

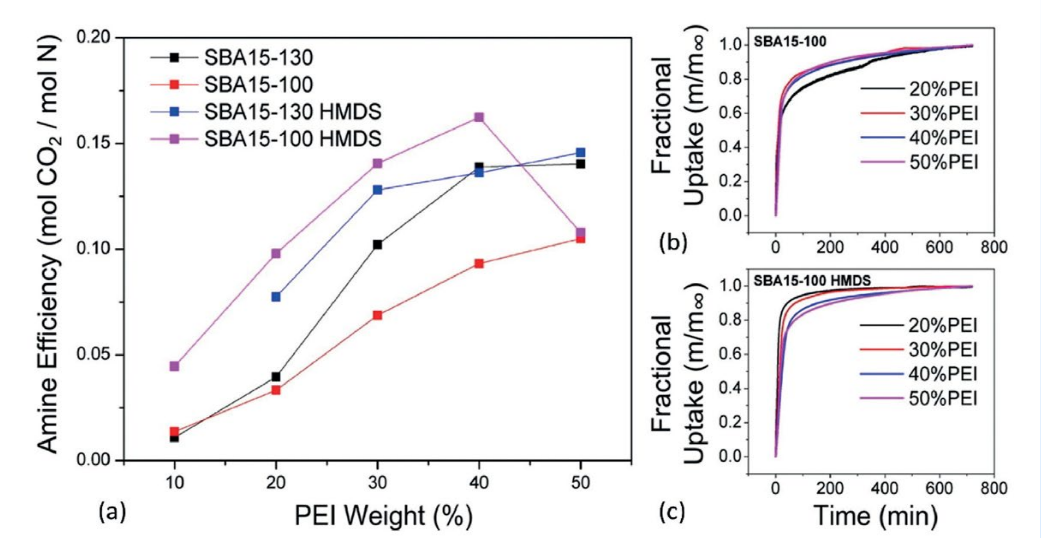
Our Technology: Porous Membrane Adsorbents with Solar Energy



Each cycle
1. Sorption
2. Desorption by heating provided by solar cell
3. Radiative cooling

- Porous membrane adsorbents
- Nanocages
- Electricity-free radiative cooling
- Solar heating and desorption

Substrates influence CO_2 sorption



Substrates:

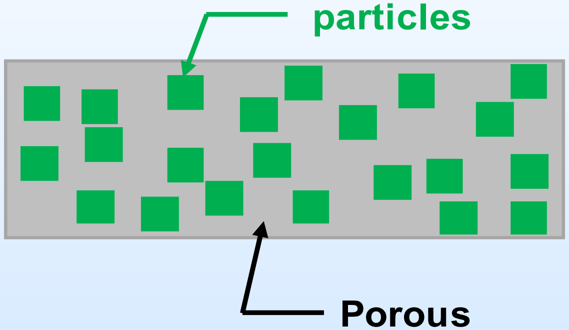
- High porosity
- High amine loading
- Low pressure drop

Porous supports	Temp. (°C)	RH (%)	CO_2 (mmol/g)	Amine-functionalized Amine (wt%)	Amine-functionalized CO_2 (mmol/g)
Fume silica	75	0	0.61	PEI(30)	3.0
SBA-15	75	0		PEI(30)	3.0
γ alumina	30	50		PEI-800(23)	1.7
MIL-101(Cr)	25	0	~0.05	PEI-800(60)	1.3
Mg_2(dobpdc)	25	0		mmen	2.0

Shi et al., *Angew. Chem. Int. Ed.* 59, 6984-7006 (2020)

Membrane Adsorbents

Flat-sheet membrane adsorbents with porosity 60 – 95% comprising CO_2-philic Self-Assembled Inorganic Nanocages (SINCs) and polymers

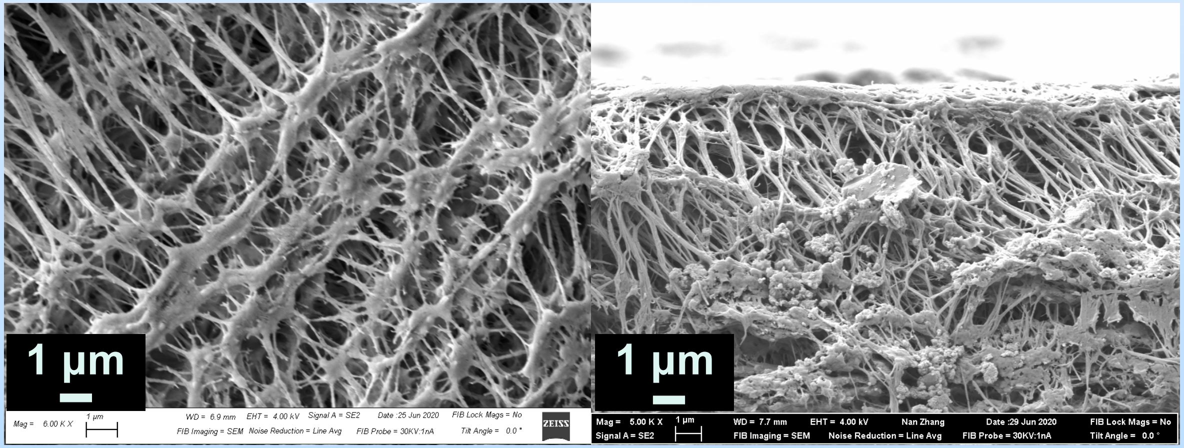


$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^-$$

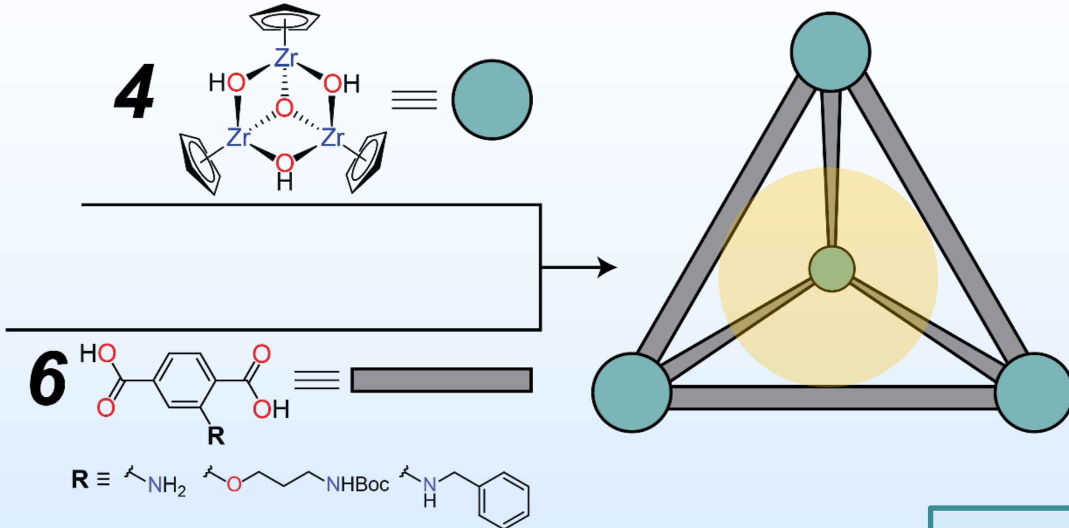
$$CO_2 + R_1R_2NH + H_2O \leftrightarrow R_1R_2NH_2^+HCO_3^-$$

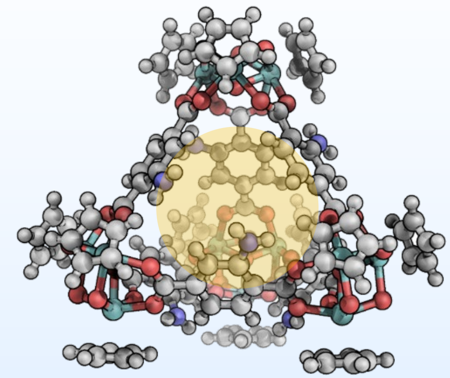
$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3^-$$



SEM photos of porous membrane

Self-Assembled Inorganic Nanocages (SINCs)

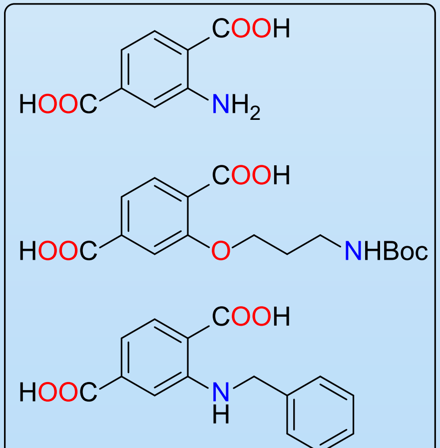




SINCs

- 2 – 5 nm in size
- Soluble in solvents
- Molecular cage analogues to MOFs – extended network solids

Current ligands



Used in gram-scale synthesis of SINCs

NH_2-cage

OPA-cage

Bn-cage

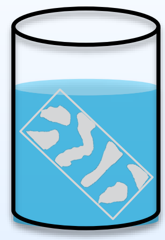
Solupor-PEI System

HDPE
Porous Support

d_p = 0.9 μm
l = 40 μm
Porosity ~ 86%

+

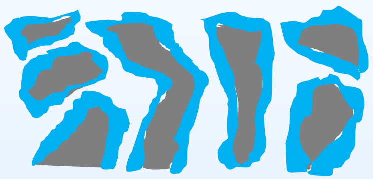
Branched PEI
MeOH solution



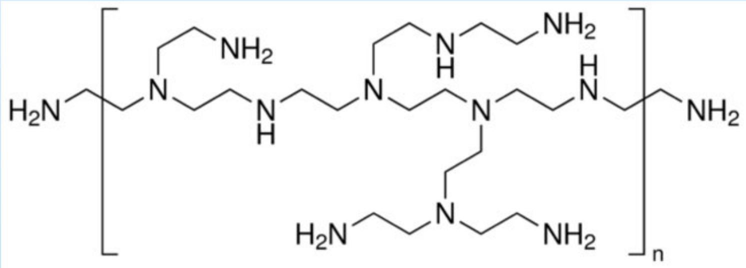
- PEI conc.: 1, 3, and 5 w/v%
- PEI Mw: 800 g/mol and 25,000 g/mol

2 hours

Supported PEI
membrane adsorbent



Branched PEI



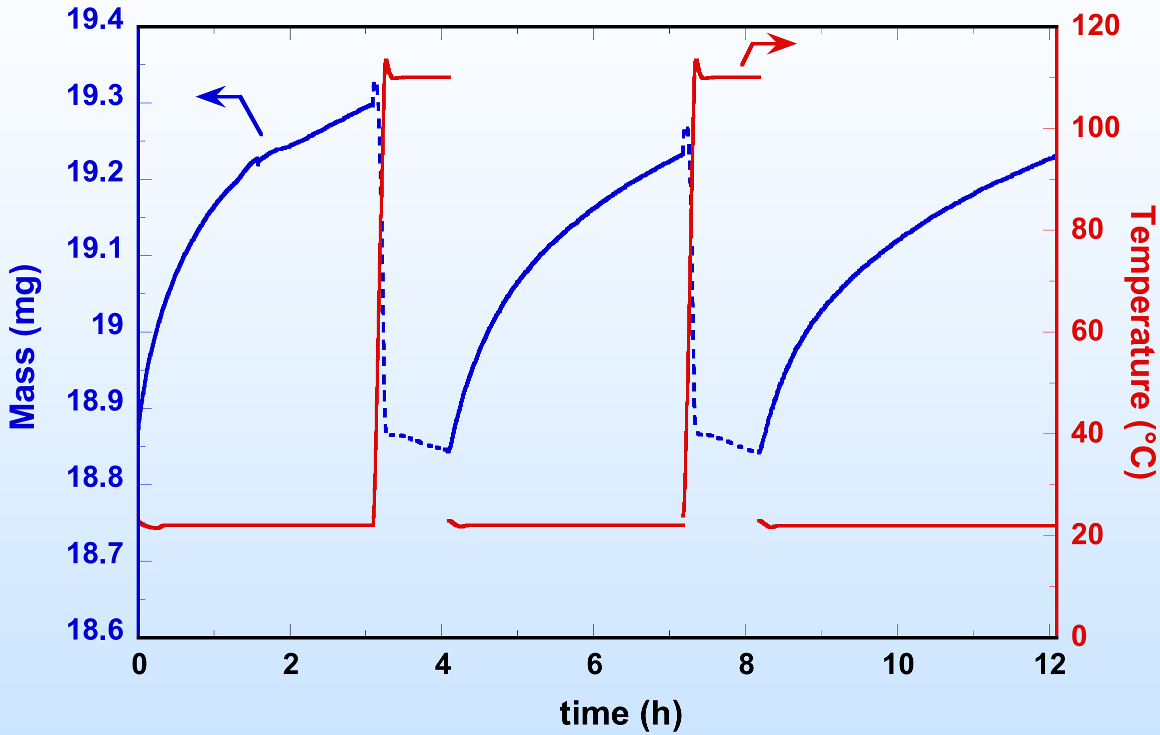
- **HDPE porous support**
  - Light weight – 5 g/m^2
  - High porosity
- **Branched PEI**
  - Higher N content – 1 mol N/ 42.8g PEI

CO_2 Sorption Capacity @ 400ppm and 22°C

Sample	PEI content (wt%)	CO_2 permeance (GPU)	CO_2 capacity (mmol CO_2/g sorbent)	Amine efficiency (mol CO_2/mol N)
Solupor	0	1.8×10^6	0.05	n/a
*s*PEI800-14	14	6.3×10^4	0.30	0.09
*s*PEI800-35	35	5.8×10^4	0.34	0.04
*s*PEI800-44	44	2.3×10^4	0.50	0.05
*s*PEI25k-16	16	6.6×10^4	0.40	0.11
*s*PEI25k-35	35	4.9×10^4	0.53	0.06
*s*PEI25k-48	48	2.3×10^4	0.51	0.05

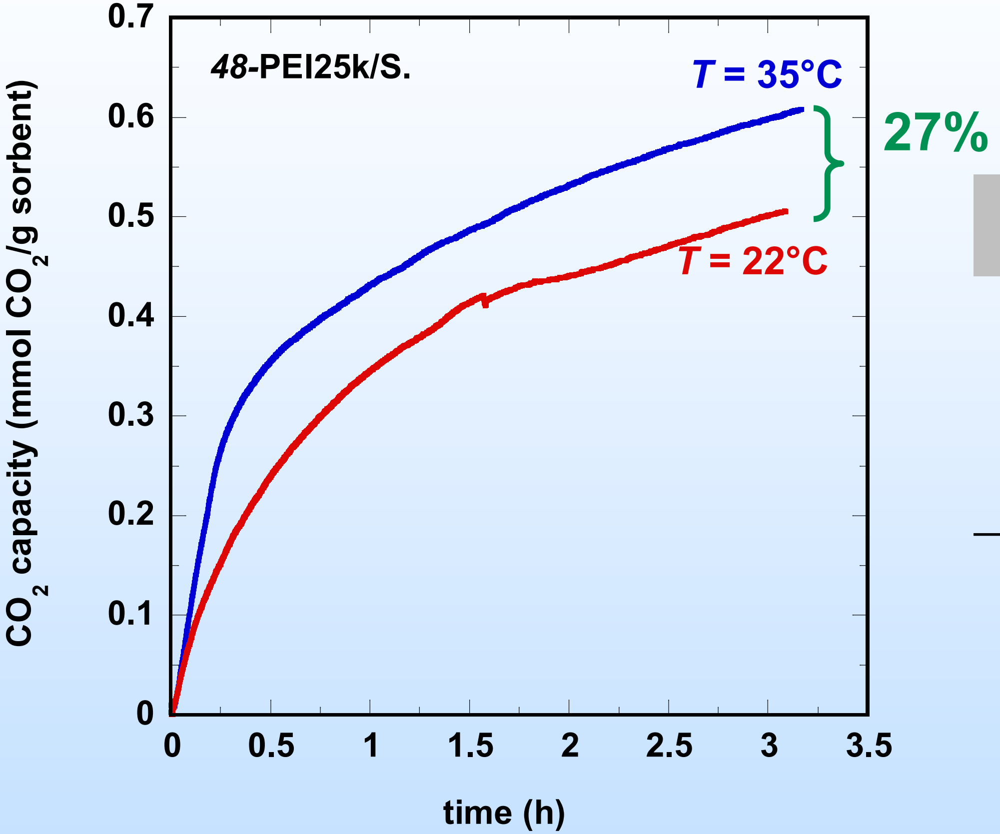
- Though both ***s*PEI800-14** and ***s*PEI25k-16** has the lowest PEI loading, they both exhibits the highest amine efficiency.
- ***s*PEI800-44** shows the highest CO_2 capacity per g of sorbent while it is the ***s*PEI25k-35** that exhibits the highest capacity.

Cycle-ability @ 400ppm and 22°C



Cycle#	CO_2 capacity (mmol CO_2/g sorbent)	Amine efficiency (mol CO_2/mol N)
1	0.51	0.05
2	0.47	0.04
3	0.47	0.04

Effect of Temperature on CO_2 Sorption Capacity



Sample	Temperature	CO_2 capacity (mmol CO_2/g sorbent)
sPEI25k-48	22°C	0.51
	35°C	0.65
	50°C	0.75
sPEI800-44	22°C	0.50
	50°C	0.96

Increasing temperature increases CO_2 capacity

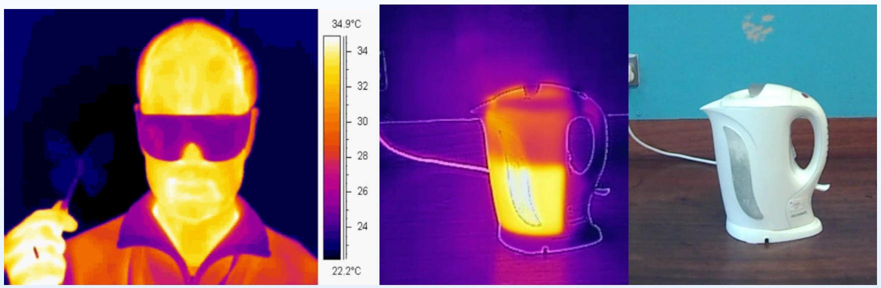
SINCs CO_2 capacity @ 400ppm and 22°C

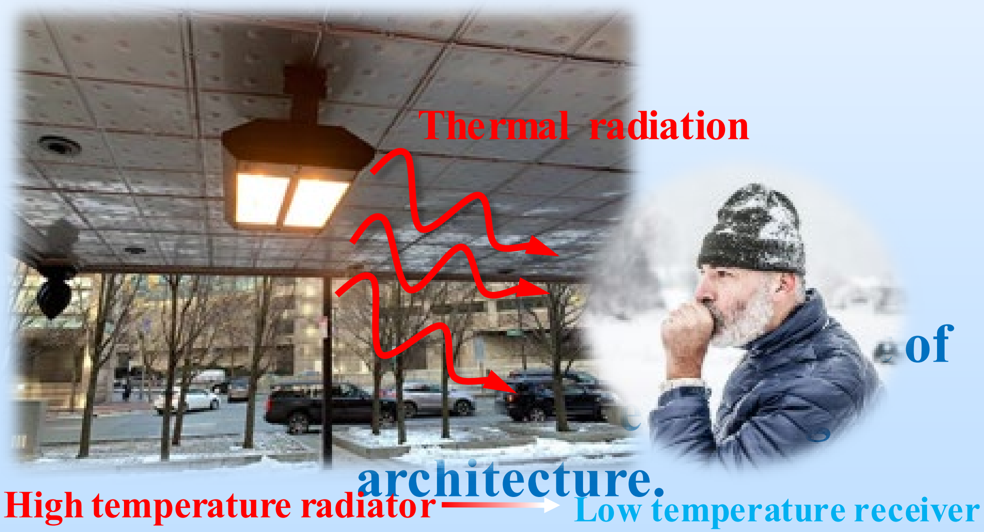
Sample	CO_2 capacity (mmol CO_2/g sorbent)
NH_2-cage	0.13
OPA-cage	0.10
Bn-cage	0.07

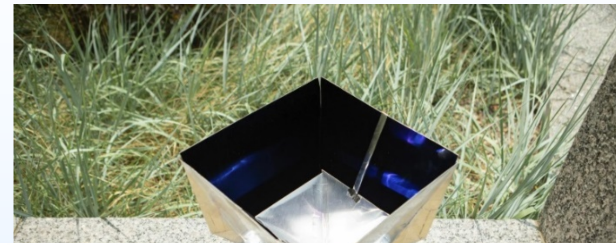
- *Solution for impregnation:*
  - 5 w/v% PEI800
  - 0.25 w/v% NH_2-cage
- *(PEI + NH_2-cage) loading* = 55 wt.%

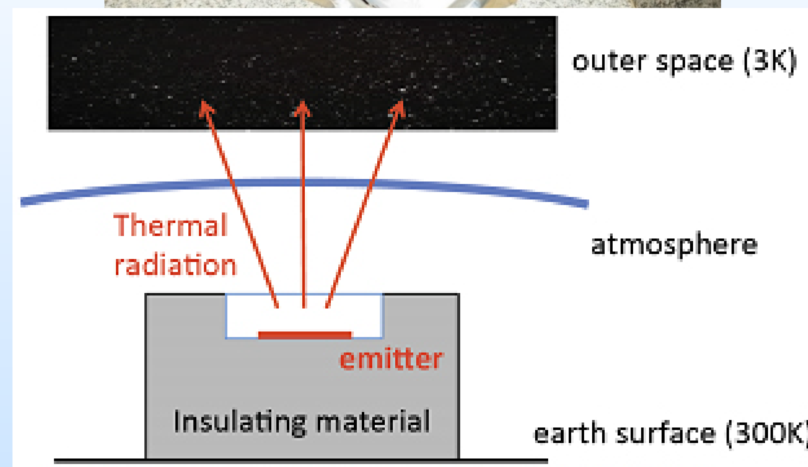
- CO_2 capacity of (PEI+NH_2-cage) = 0.58 mmol CO_2/g
- 16% increase as compared to *s*PEI800-44 (i.e. 0.50 mmol CO_2/g)

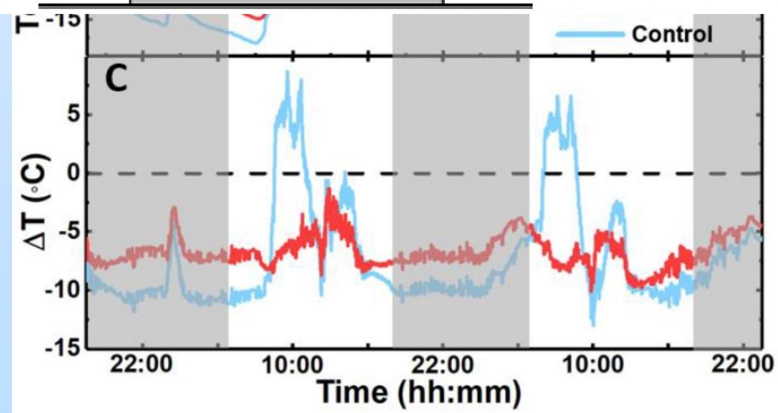
Radiative Cooling
An Electricity-Free Cooling Technology











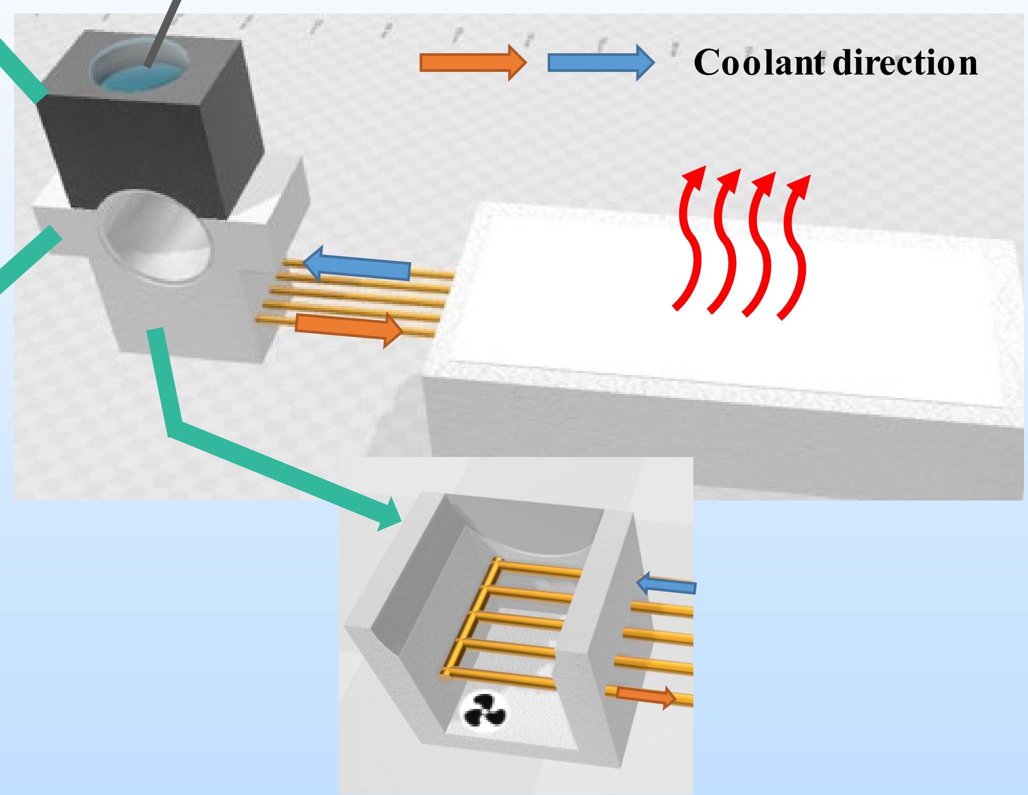
Gan, et al., *Nat. Sustain.* **2**, 718 (2019)

Prototype Design

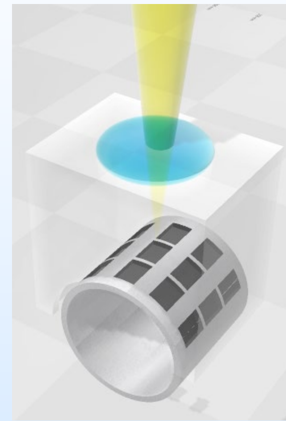
Desorption chamber

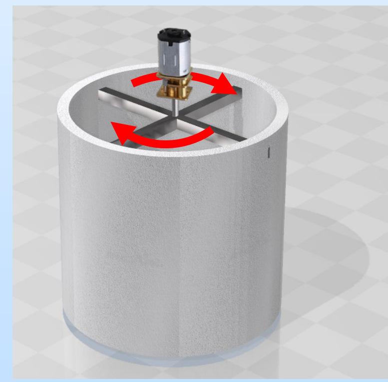
One or multiple Fresnel lens will be employed to focus solar light to heat the sample.

Thermal insulation



Adsorption chamber





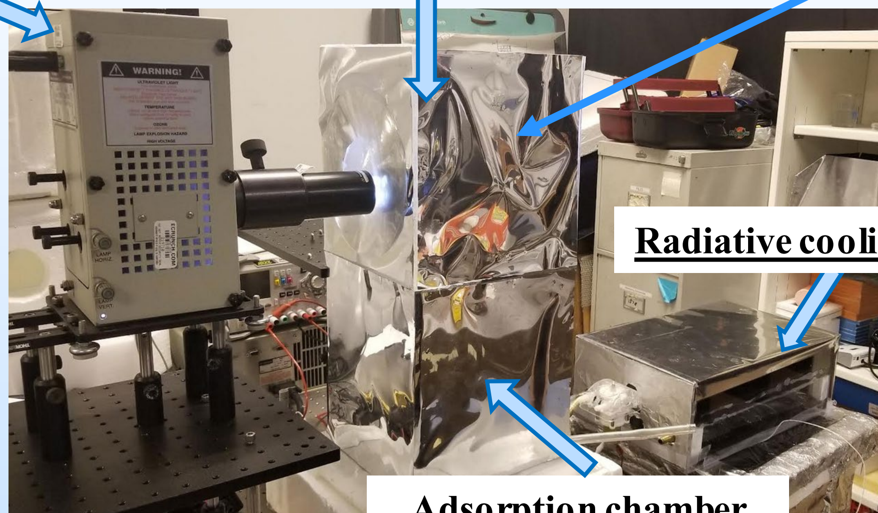
Rotation tube
(with sample container)

System Assemble

Solar Simulator

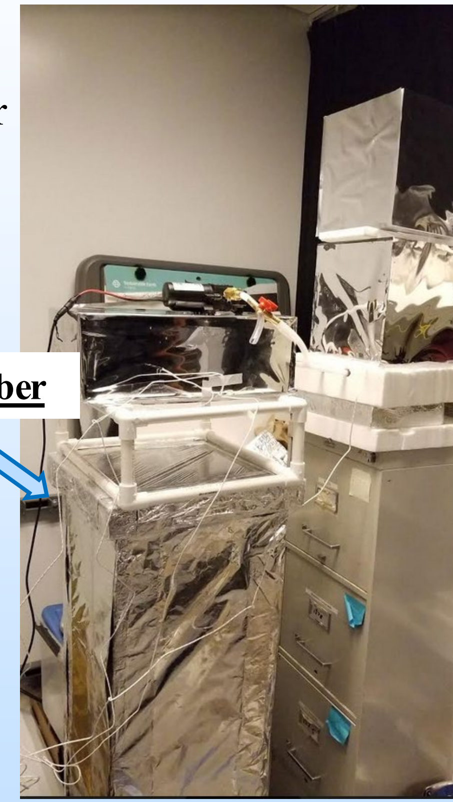
Desorption chamber

Thermal insulating shelter

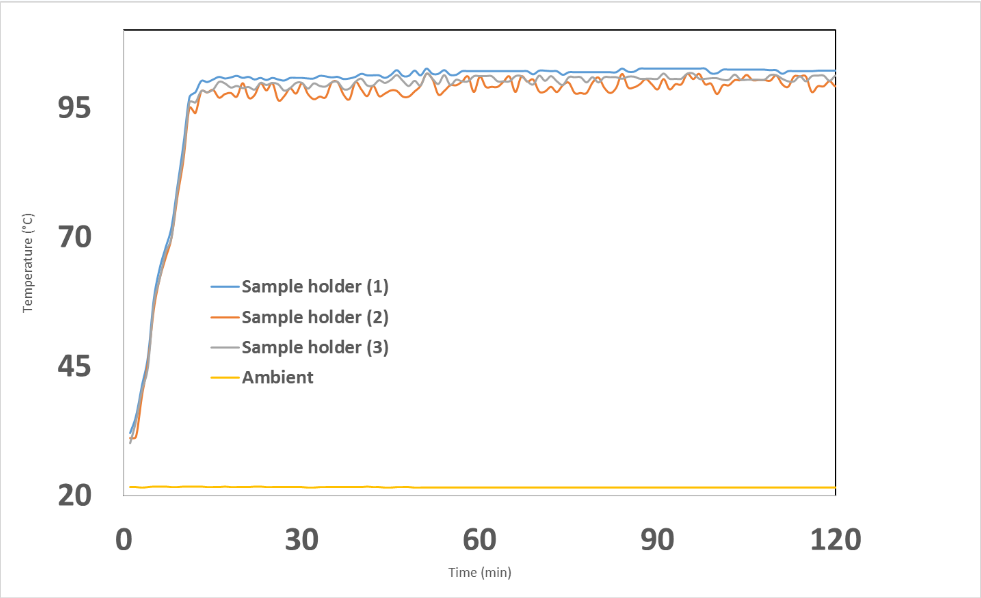


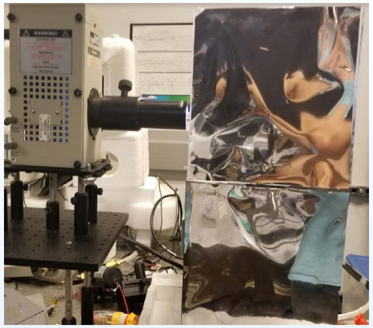
Radiative cooling chamber

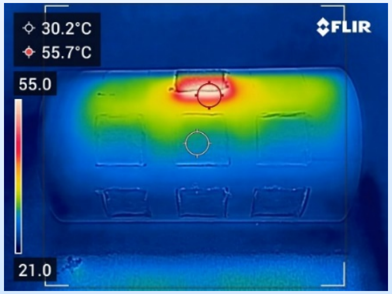
Adsorption chamber



Sample Holder Heating Test

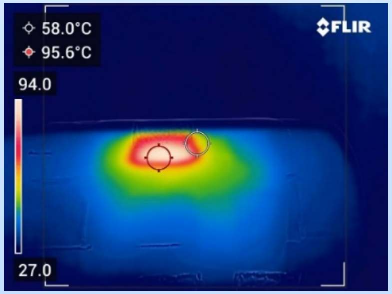






<u>Without Fresnel lens</u>

Temp. = 55.7 °C

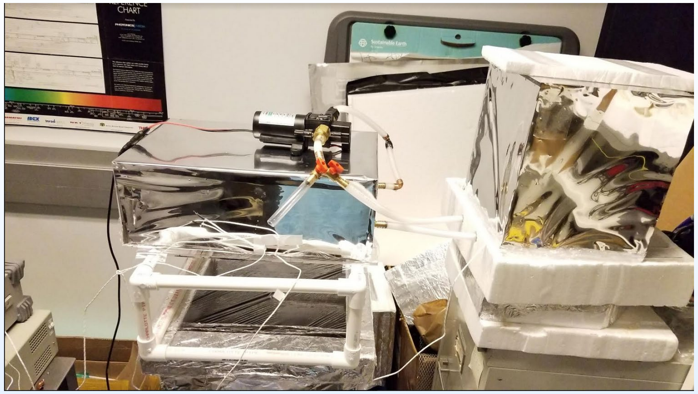


<u>With Fresnel lens</u>

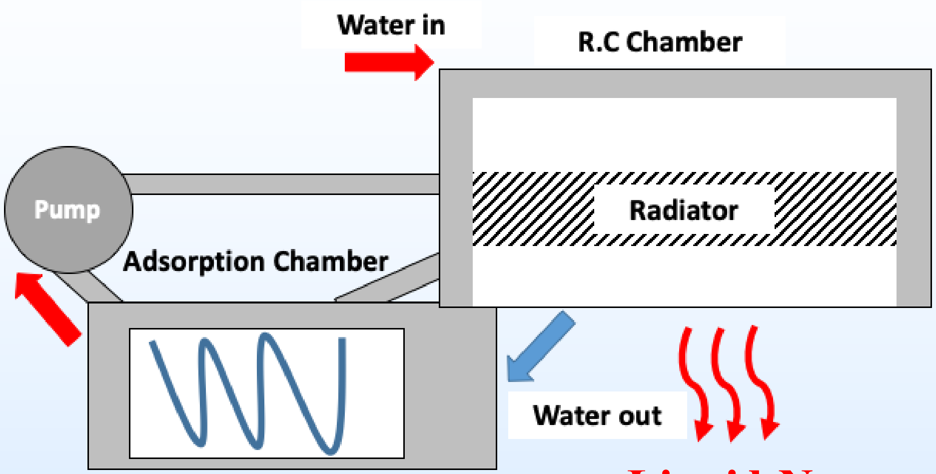
Temp. = 95.6 °C

- Carbon black coating allows for high absorption of solar radiation.
- Focusing sunlight with Fresnel lens increases temperatures significantly.

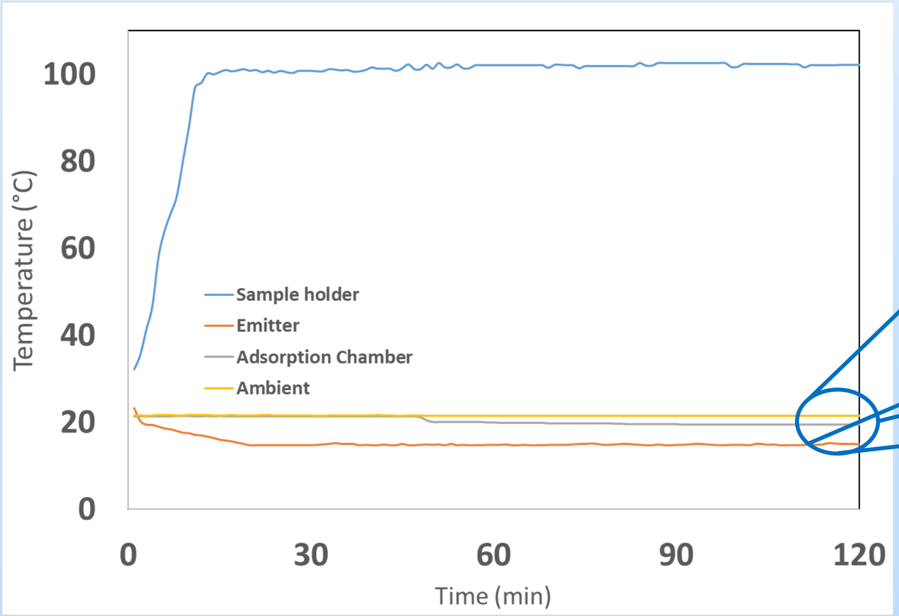
Preliminary Cooling Evaluation



Emitter reaches ~ 14.5°C,
ambient ~ 22°C



Liquid N_2



Adsorption chamber is
~ 2°C below ambient

Trimeric Corporation (Trimeric)

- Privately-owned consulting firm located in Buda (Austin), Texas
- Provides technical services (i.e., expertise in the form of labor hours) to private industry and government-funded clients
- Specializes in process chemical engineering and R&D
  - 18 process chemical engineers, plus access to very experienced experts
- Is independent of licensed technologies or chemicals – an unbiased advocate for our clients with a technology-neutral position

- **Andrew Sexton:** CO_2 Project Experience (Capture, Purification, Dehydration/Compression, Pipelines, Liquefaction)
  - **Evaluation of PSA and TSA process options for sorbents under previous DOE funded projects and for commercial clients**
  - **DAC process design experience for commercial client**

Summary

- Membrane adsorbents exhibits CO_2 capacity ~ **0.5 mmol CO_2/g** at 400ppm CO_2 in Air and 22°C.
- Increasing temperature from 22°C to 50°C results in **50% - 100% higher CO_2 capacity and amine efficiency.**
- Various SINCs were synthesized and found to increase CO_2 capacity of membrane adsorbent.
- A working prototype for solar heating and radiative cooling were developed.

Future Plan

- Synthesize high amine-content SINCs.
- Further incorporate the most promising SINCs into membrane sorbent.
- Evaluate the effect humidity on CO_2 capacity.
- Carry out radiative cooling/heat outside.
- Assemble a functional prototype with the best membrane adsorbent
- Conceptual process design and TEA

Thank you for your attention!

Appendix

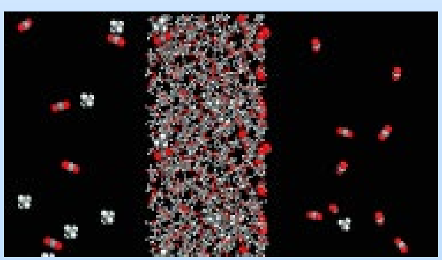
Project Timeline

Research Tasks	Month (10/2020 – 03/2022) 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
1. Project management and planning	35%
2. Optimize porous support	100%
3. Synthesize and characterize SINCs	50%
4. Prepare membrane adsorbents	40%
5. Characterize membrane adsorbents	60%
6. Design and construct a prototype with rapid cooling and heating for adsorption/desorption cycle	35%
7. Lab-scale demonstration of continuous DAC	0%
8. Conceptual process design and TEA	10%

Team and Facilities

Haiqing Lin

Novel membrane materials for CO_2 capture

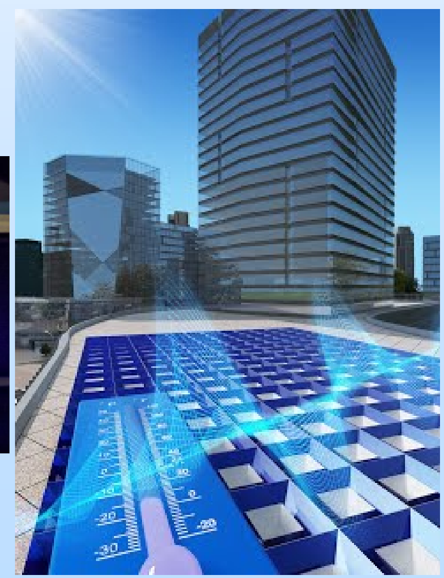


Tim Cook

Self-assembly of discrete inorganic metallacycles & cages

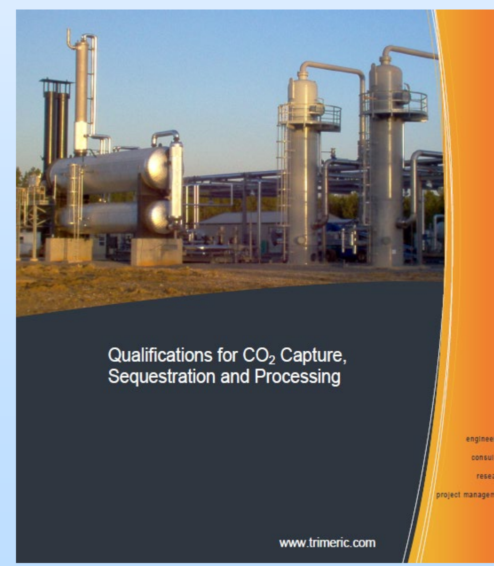
Qiaoqiang Gan

Thermal management



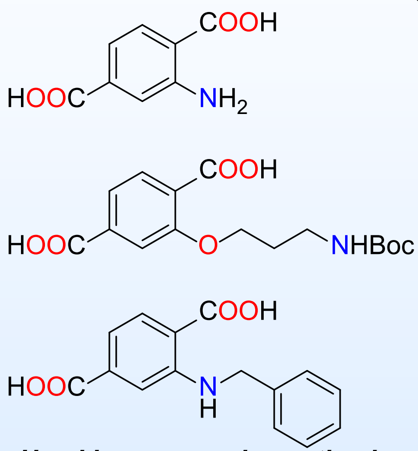
Andrew Sexton

TEA



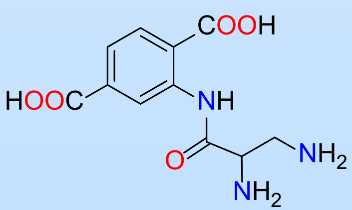
Developing a library of amine-bearing ligands for self-assembly

Current ligands

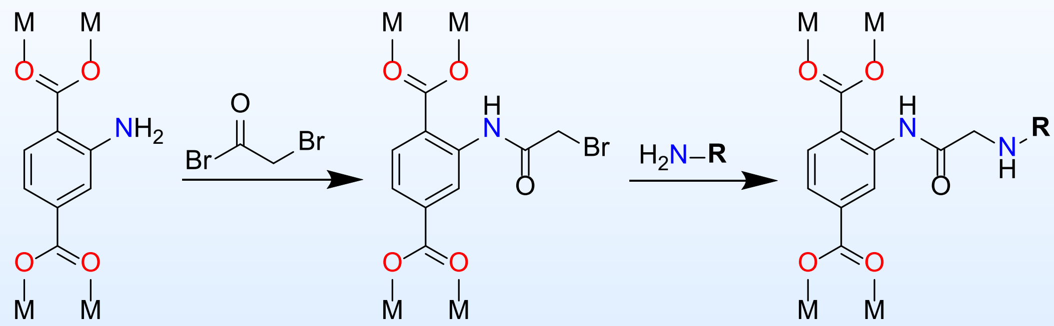


Used in gram-scale synthesis of SINCs

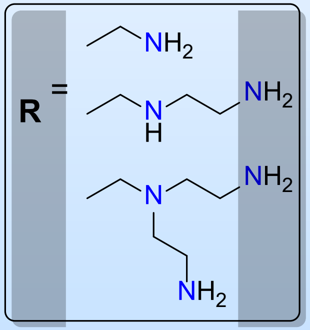
Ligand in progress



Upcoming – Adapting a route to post-synthetic modification



We continue to expand the *library of ligands* used to ***increase amine-site density***.



Post-synthetic modification circumvents challenges posed by *acid-base interactions* between ***amines*** and ***carboxylic acids***.

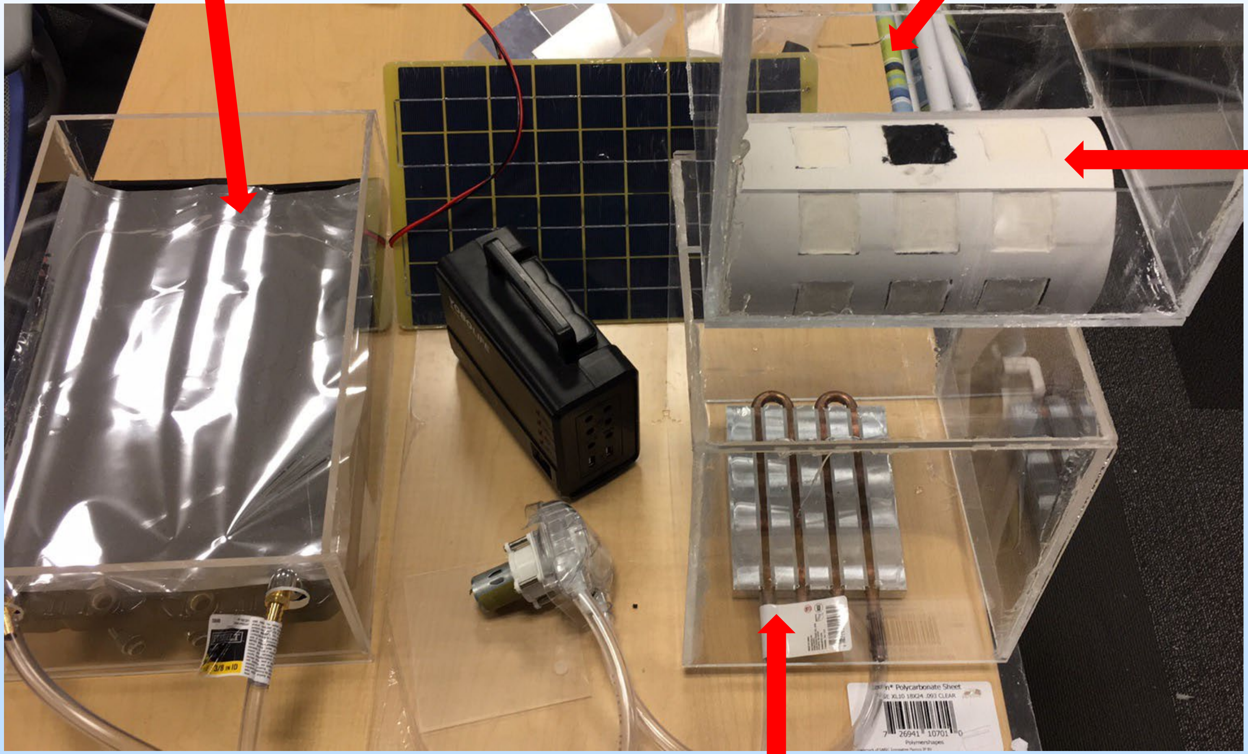
Post-synthetic modification adapted from: Queen, W. L., *Inorg. Chem.* **2021** *ASAP.*

Build

Part 3. Desorption chamber

Part 1. Radiative cooling chamber

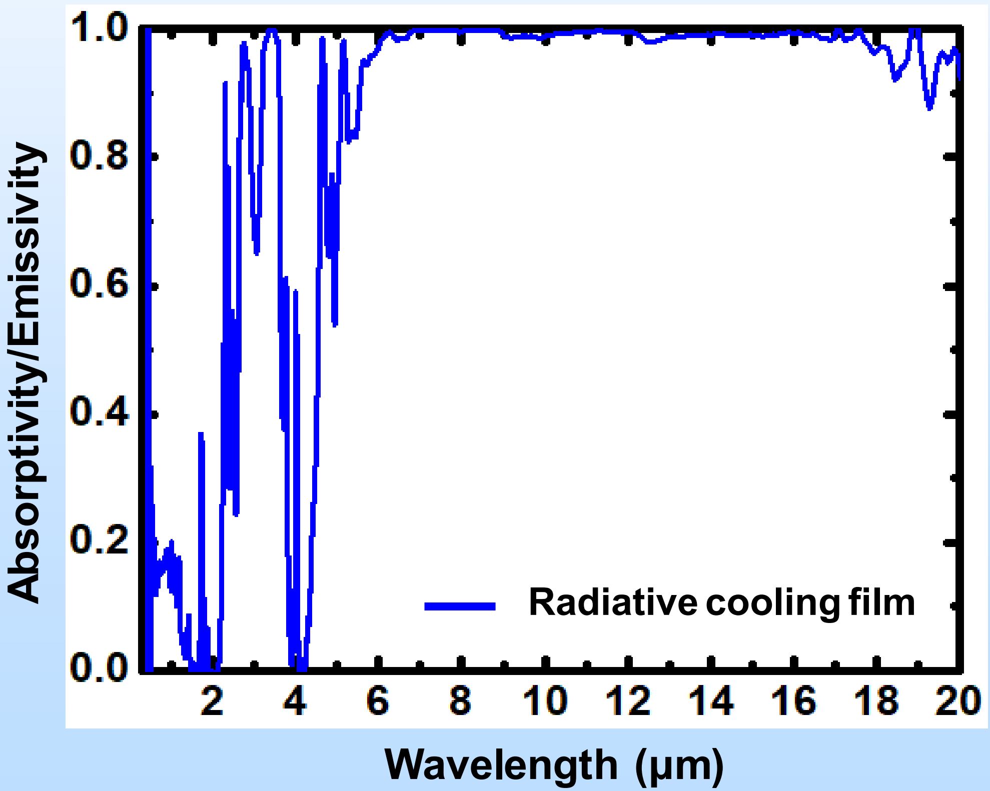
Part 4. Rotation tube

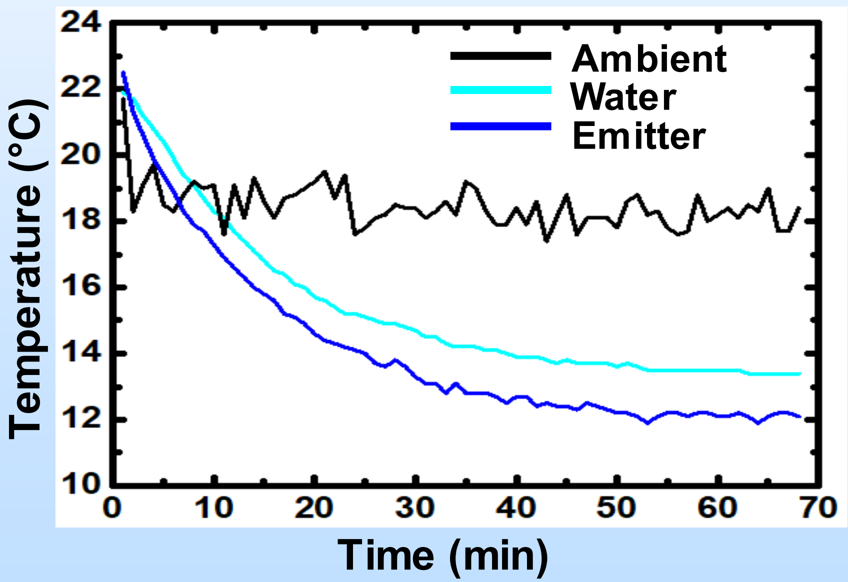


Part 2. Adsorption chamber

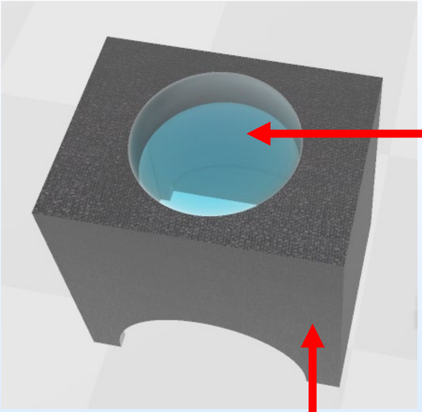
Radiative Cooling Film Spectrum

- Current radiative cooling (r.c.) film has near unity emissivity in atmospheric window (7-13μm)
- Allows for near ideal thermal transfer & cooling





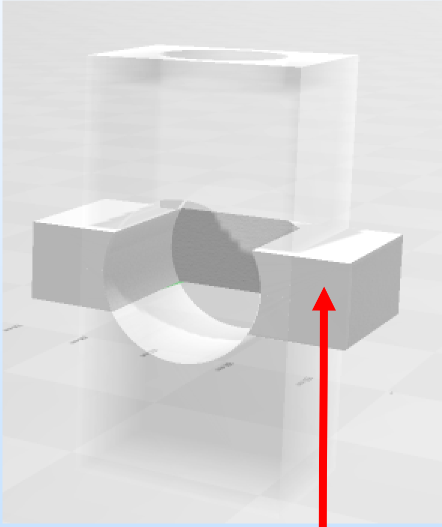
Desorption chamber



One or multiple Fresnel lens will be employed to focus solar light to heat the sample.

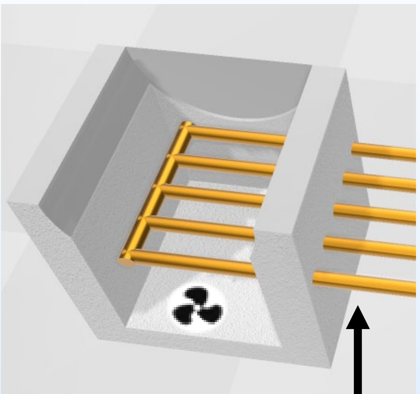
Black coating will be painted to preheat the chamber.

Thermal insulation



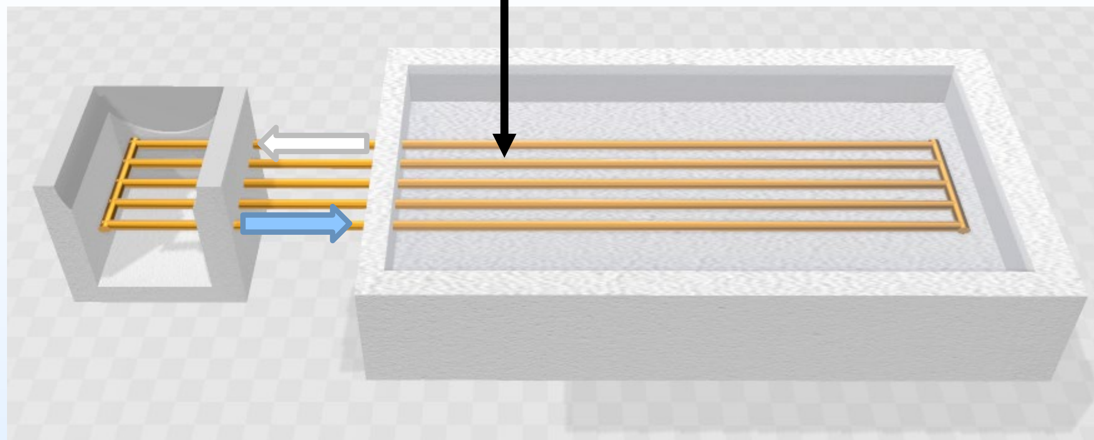
A thermal insulation layer will be employed to ensure the temperature gradient between desorption chamber and absorption chamber.

Absorption chamber

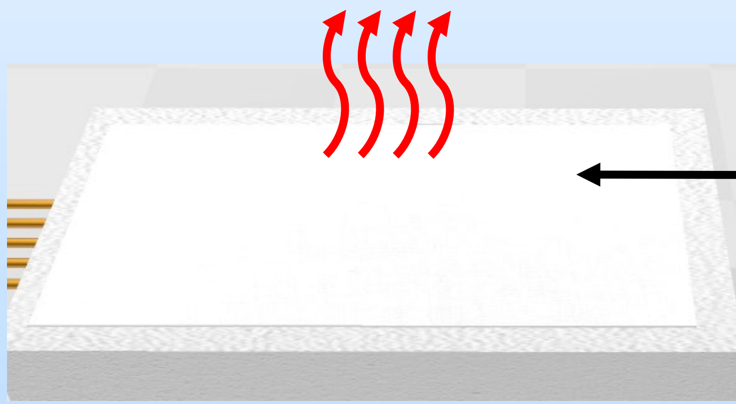


- Cold coolant will be transported to the desorption chamber. When cooperated with fans, the temperature inside the desorption chamber will be lowered.

- The coolant will be circled back to the cooling chamber, driven by a water pump.



Coolant direction

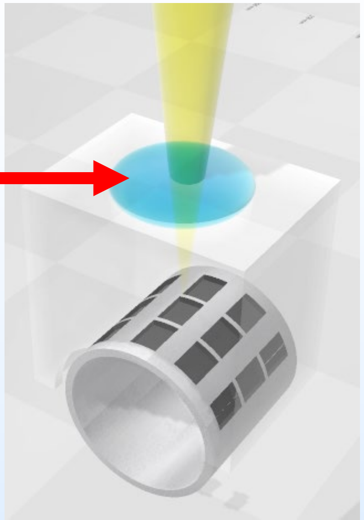


- A polymer thin film will coat the chamber and release the heat via thermal radiation, thereby reducing the temperature.

Cooling chamber

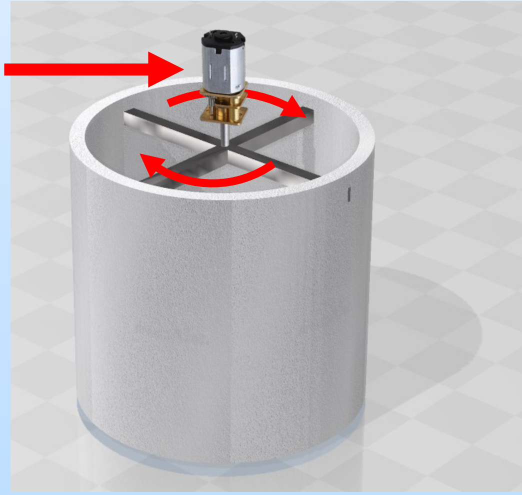
Rotation tube (sample holder)

- Light will be concentrated by the Fresnel lens and heat the sample holder.

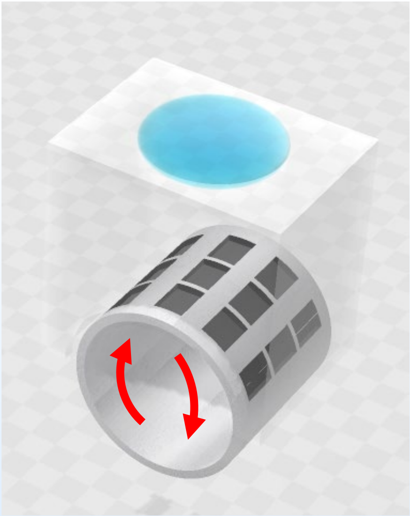


Samples will be attached in each individual box and heated by the black coating.

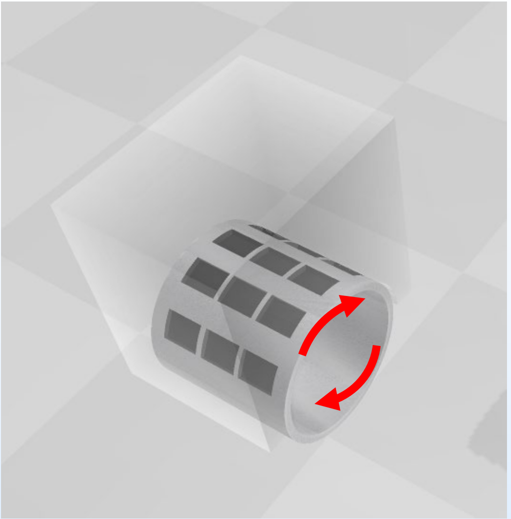
- A gear motor will be fixed on the bottom and rotate the tube.



Heating/Desorption



Cooling/Adsorption



- Samples will be contained in each individual box. When functioning, a gear motor will rotate the tube and transport the samples between two chambers;
- In the desorption/heating process, solar light will be focused by Fresnel lens and heat up the black coating in the sample container. The temperature of the samples will rise rapidly, therefore releasing CO_2;
- In the adsorption/cooling process, the cold coolant cooled by radiative cooling will be cooperated with a fan to reduce the temperature. The temperature of the samples will be decreased, therefore enabling CO_2 capture.