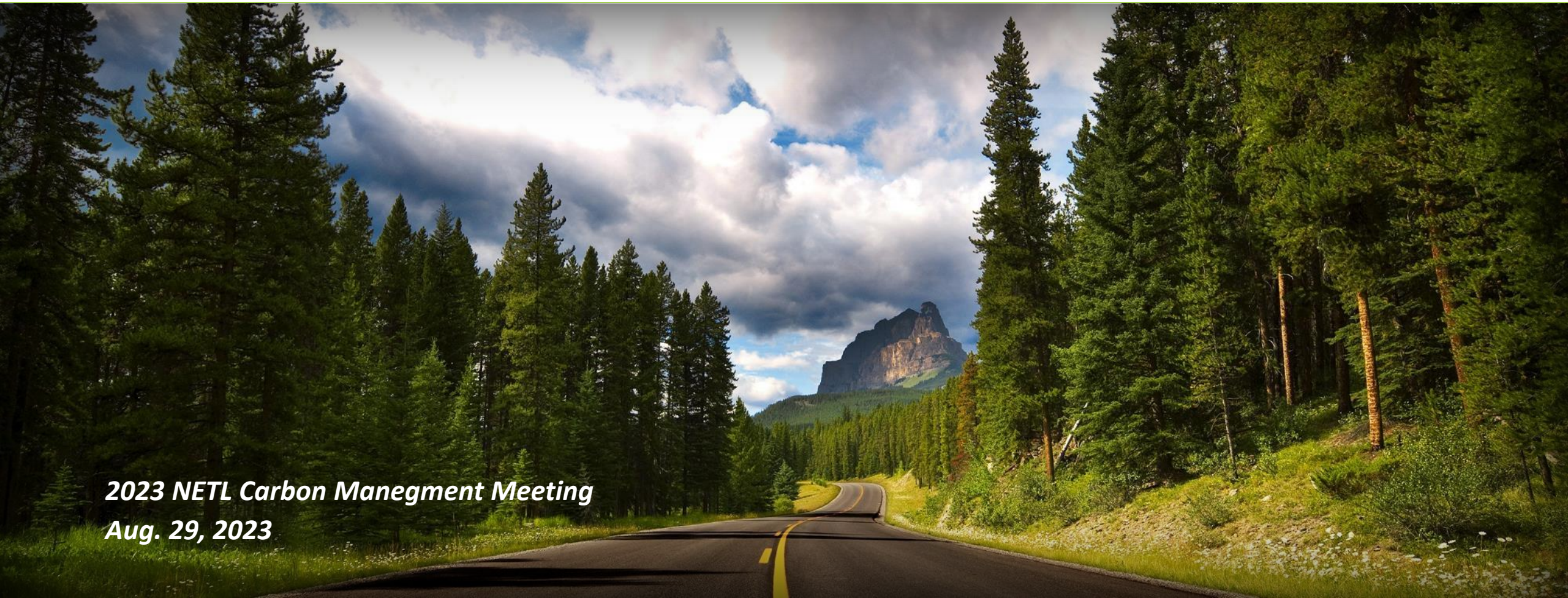
Polymer Sorbents Fibers for Direct Air Capture

Ali Sekizkardes
Research Scientist



2023 NETL Carbon Manegment Meeting
Aug. 29, 2023

Disclaimer

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Authors and Contact Information

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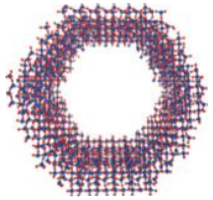
[c]*NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236*

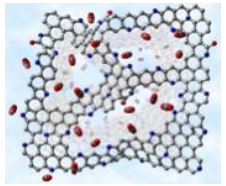
Research Objective

Adsorbent Portfolio

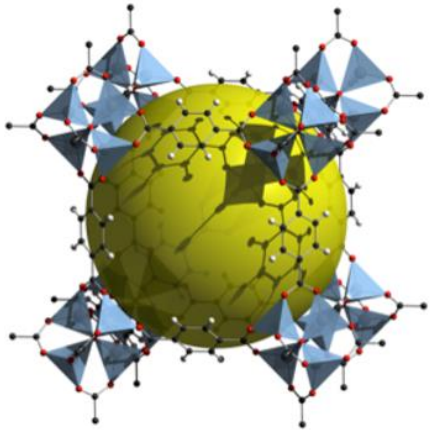
Zeolites



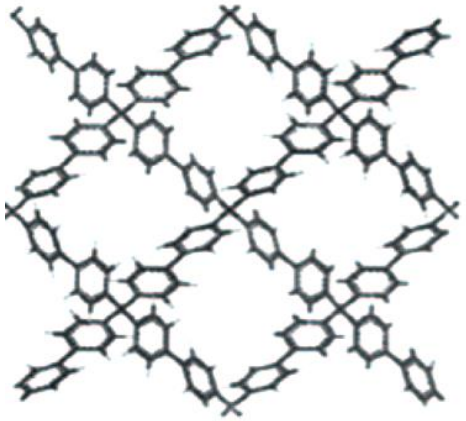
Silicates



Porous Carbon



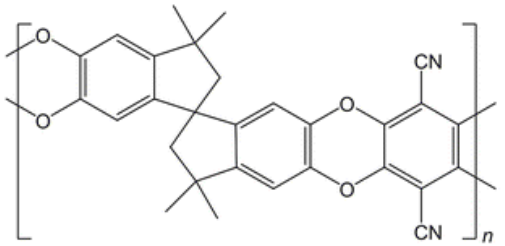
MOFs

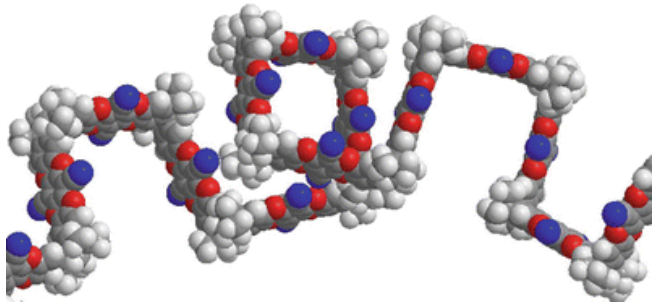


Porous Polymers

1990 2000 2010 Timeline

Chem. Rev. **2017**, 117, 1515−1563





Polymers of Intrinsic Microporosity (PIM)

N. B. McKeown and P. M. Budd,
Chem. Soc. Rev., **2006**, 35, 675–683

DAC Sorbents

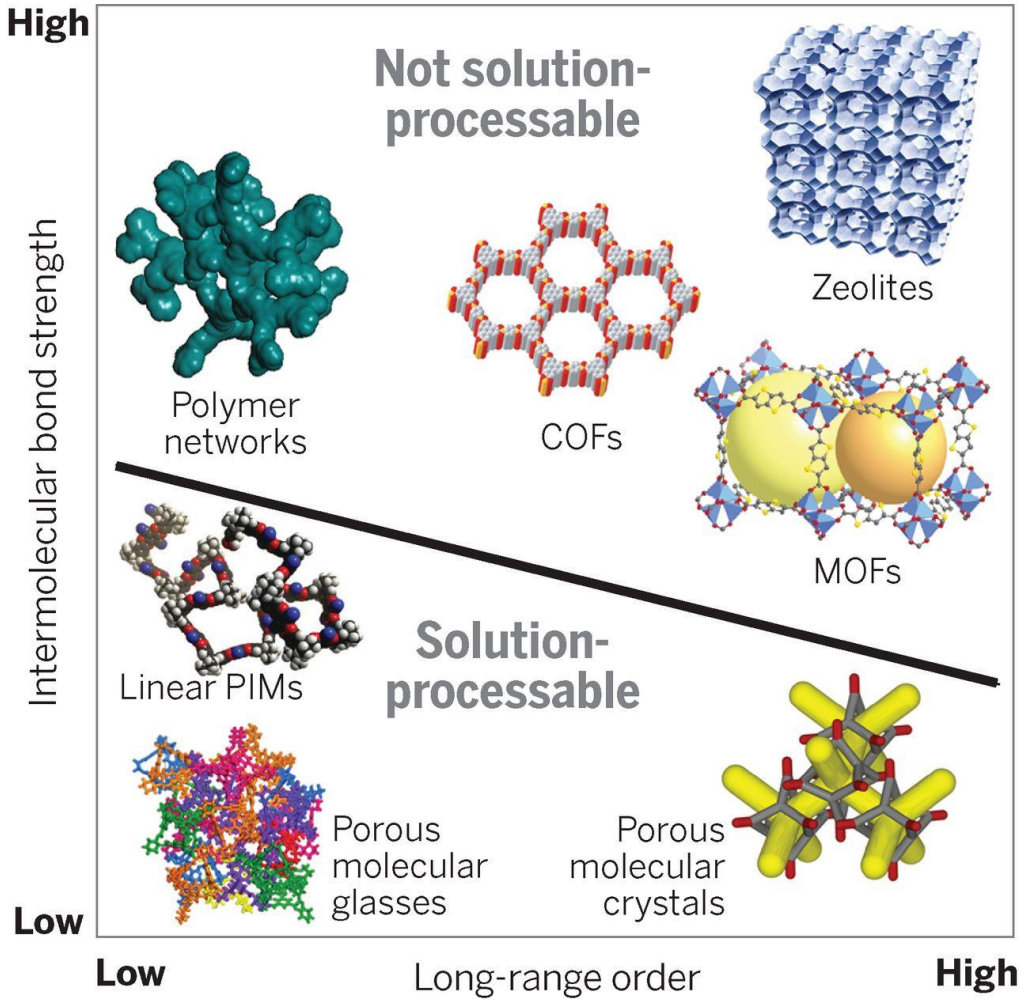
high CO_2 uptake

fast kinetics

low-energy regeneration

cyclability

processibility



Cooper et al. *Science* **2015**, 348, 6238

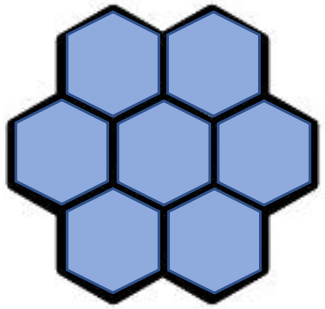
"Targeted geometries can have 10-20 times less pressure drop compared to packed reactors"

Technology Background: Aminated Sorbents

macro porous particle (SA= 100-200 m^2/g)

amine impregnation

polyamines

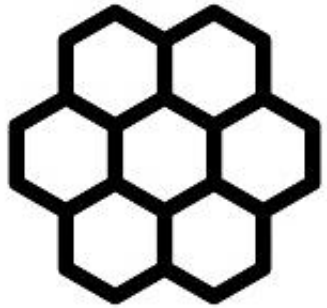


amine impregnated sorbent

- high CO_2 uptake
- high polyamine loading (50%)
- slow CO_2 diffusion
- regeneration (>100 °C)
- less amine leaching
- oxidation problem

Energy Environ. Sci., **2022,** 15, 1360-1405

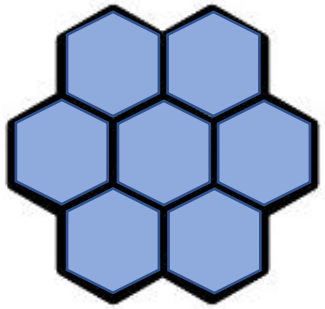
Technology Background: Aminated Sorbents



macro porous particle (SA= 100-200 m^2/g)

amine impregnation

polyamines



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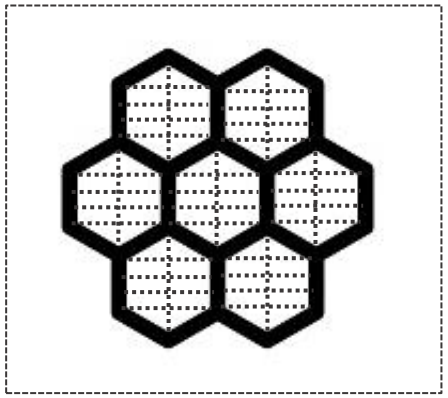
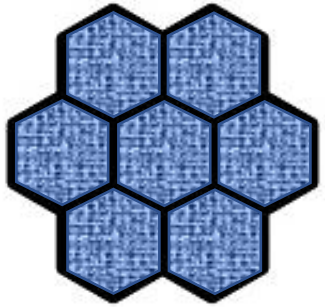
Energy Environ. Sci., **2022,** 15, 1360-1405



nano porous particle (SA= 500-2000 m^2/g)

amine impregnation

molecular amines

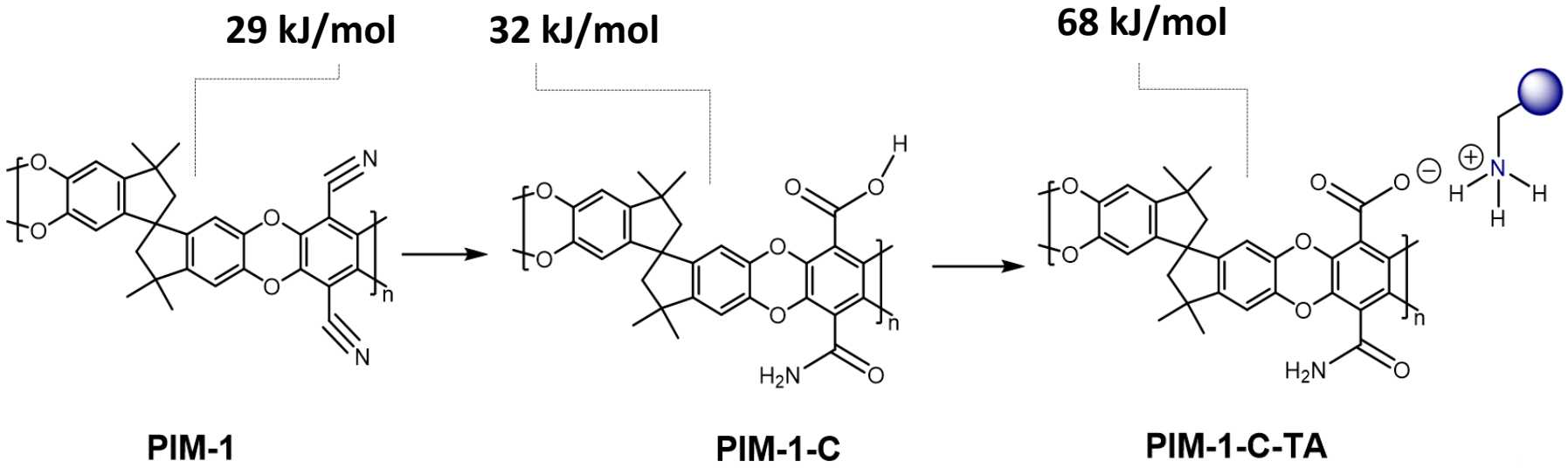


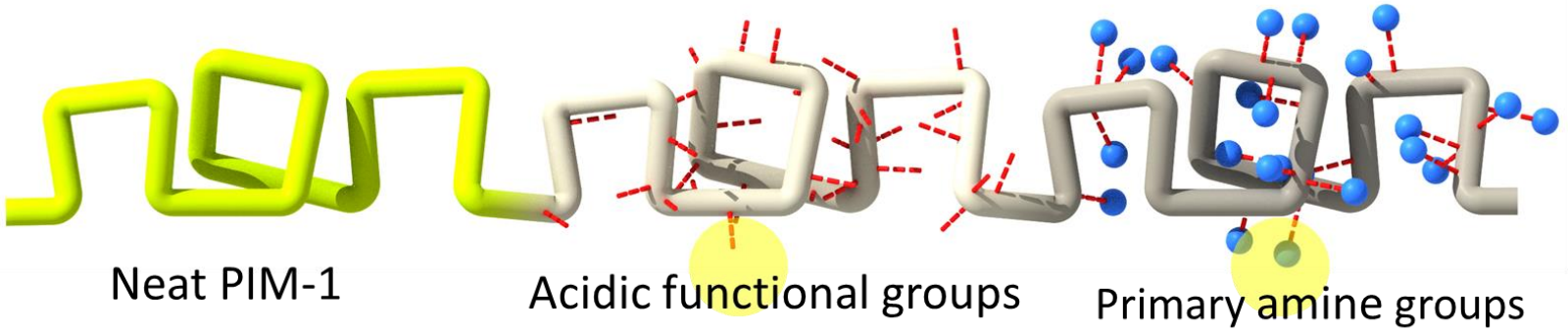
amine impregnated sorbent

- High CO_2 uptake
- molecular amine (<30%)
- faster CO_2 diffusion
- Regeneration (<100 °C)
- amine leaching
- limited oxidation

Mater. Adv., **2021**, *2*, 5843-5880

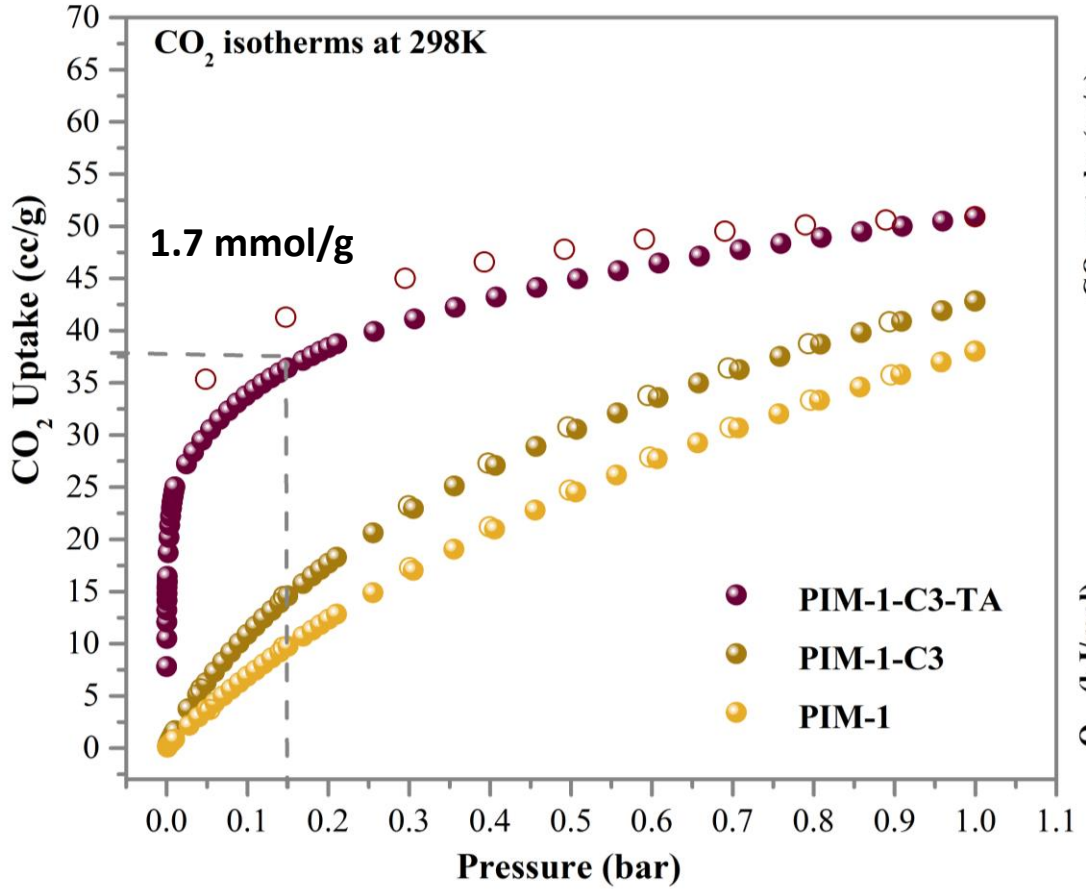
Processible Polymeric Sorbent Concept

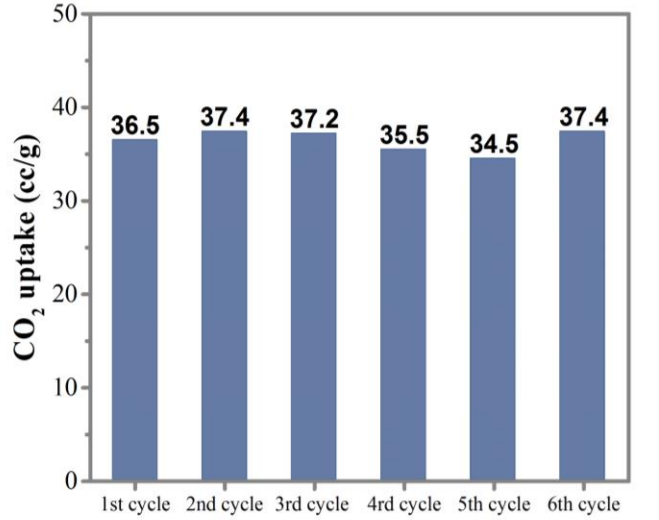


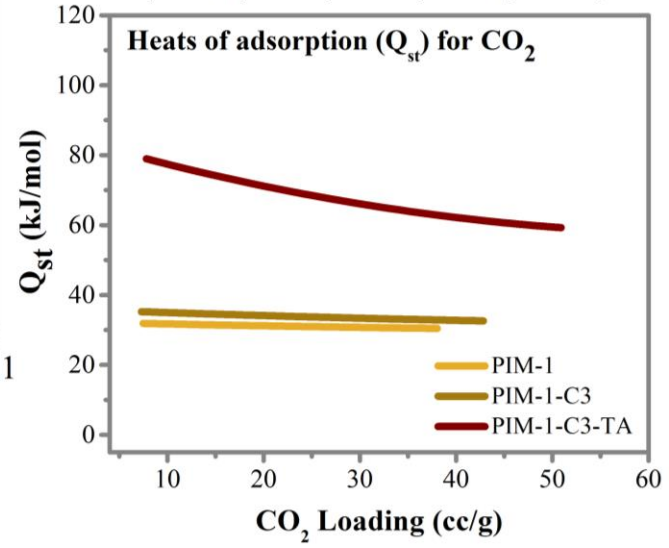


Sekizkardes, A. K.; Hammache, S.; Hoffman, H. S.; Hopkinson, D. ACS Appl. Mater. Inter. **2019**, 11, 30987−30991

Processible Sorbent Concept

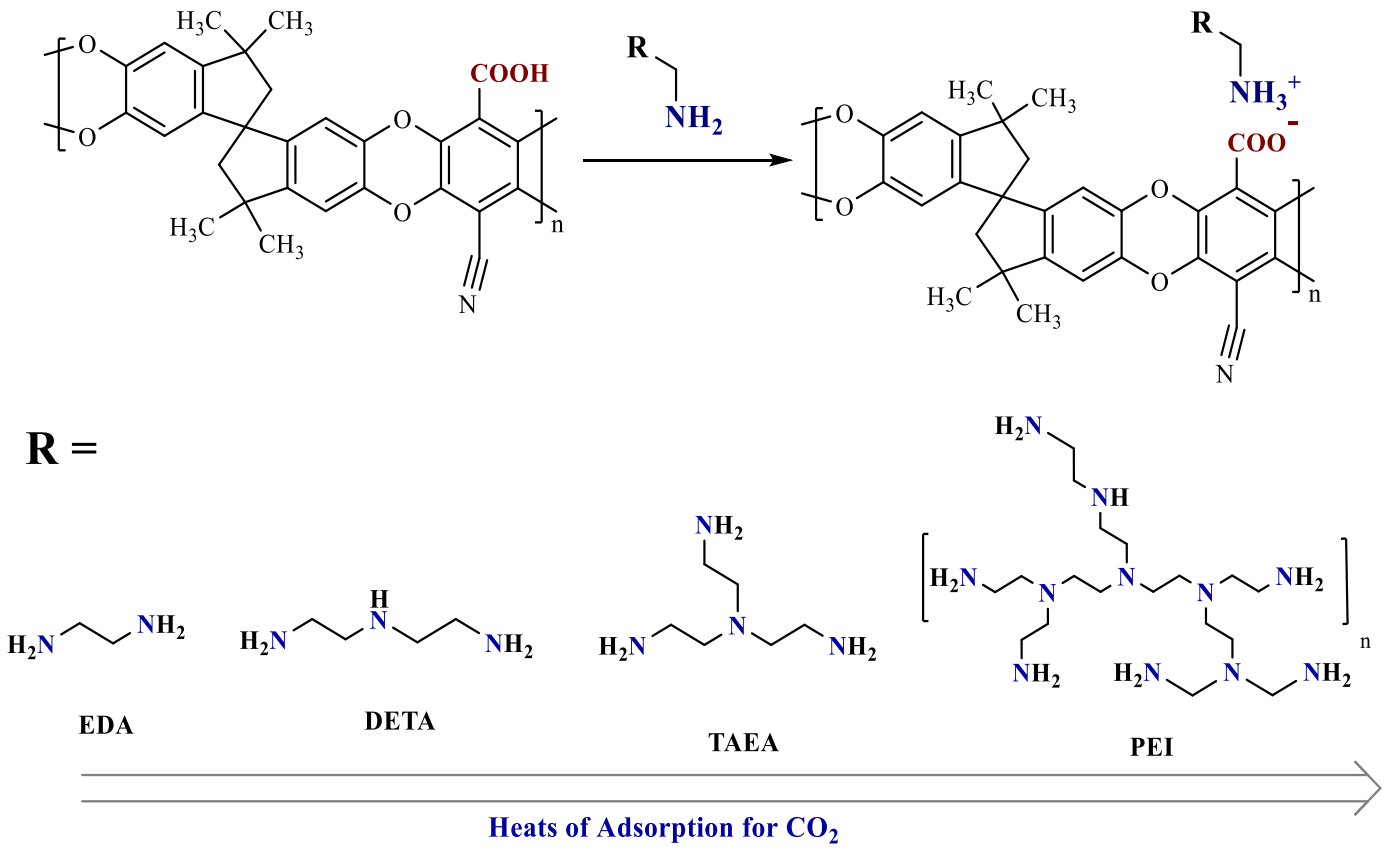






Sekizkardes, A. K.; Hammache, S.; Hoffman, H. S.; Hopkinson, D. ACS Appl. Mater. Inter. **2019**, 11, 30987−30991

Processible Sorbent Concept

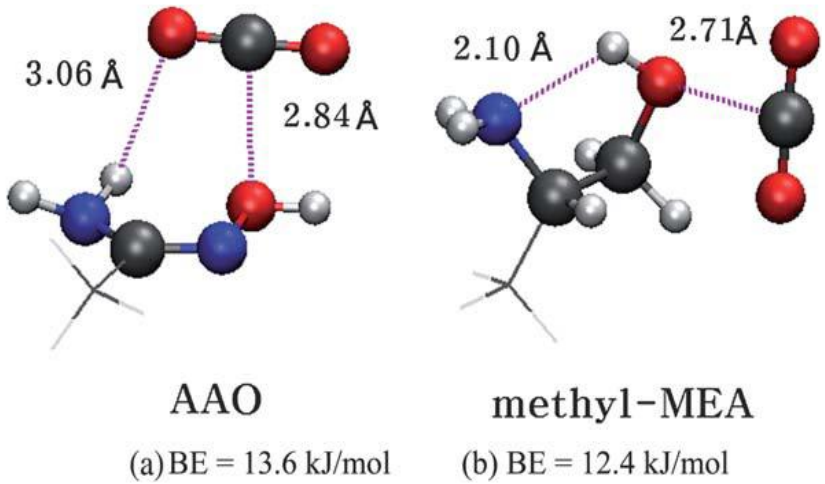


- Can be scaled up with cost-efficient synthesis
- Soluble in common solvent and can be processed
- Tunable chemical structure
- High surface area and pore volume
- Library of different sorbents can be prepared

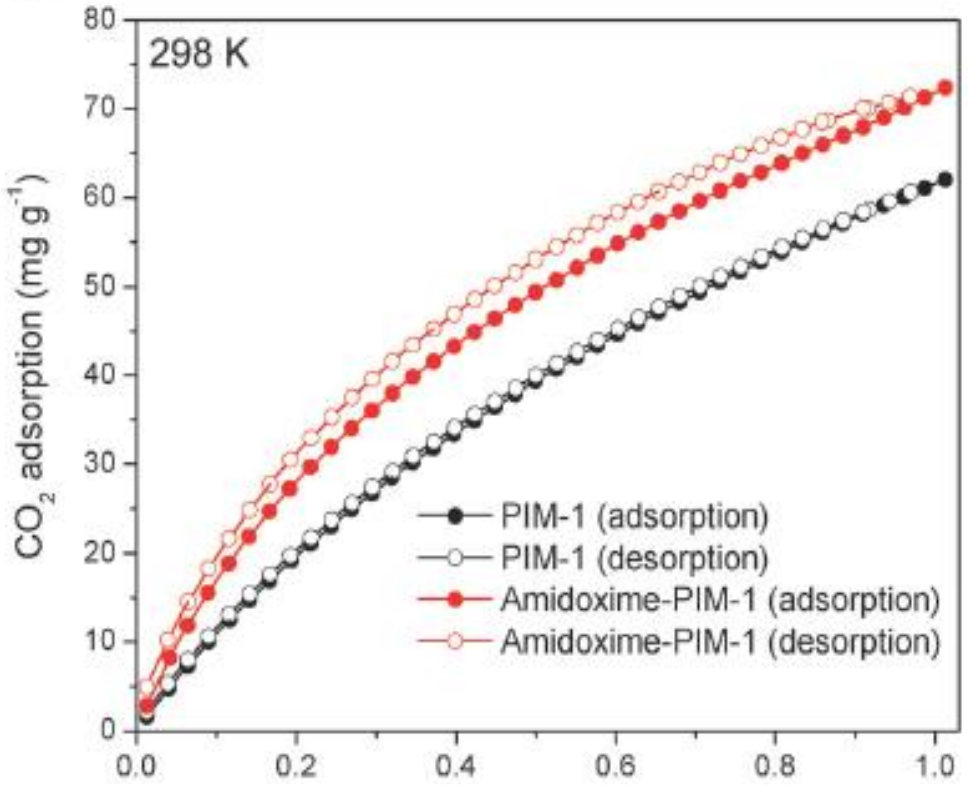
Sekizkardes, A. K. and Hopkinson, D. US Patent 2022 0032268A1

Amidoxime Functionality

- Amidoxime functionality for amine tethering

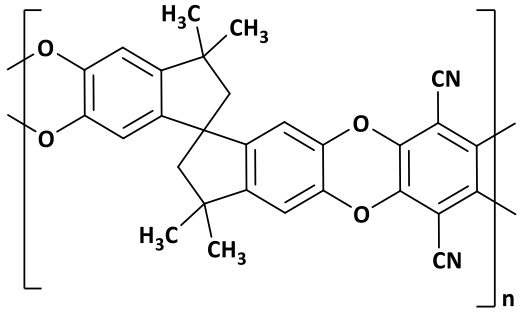


Energy Environ. Sci., **2011**, *4*, 4528–4531



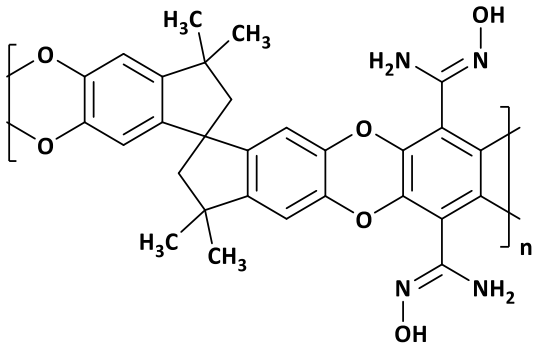
Chem. Commun., **2012**, *48*, 9989-9991
by Cafer Yavuz group

Amidoxime Functionalized PIM-1



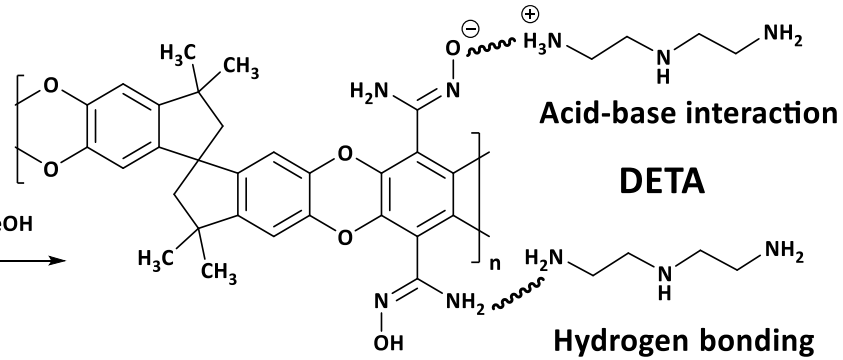
PIM -1

NH_2OH, MeOH



PIM -1-AO

DETA, MeOH



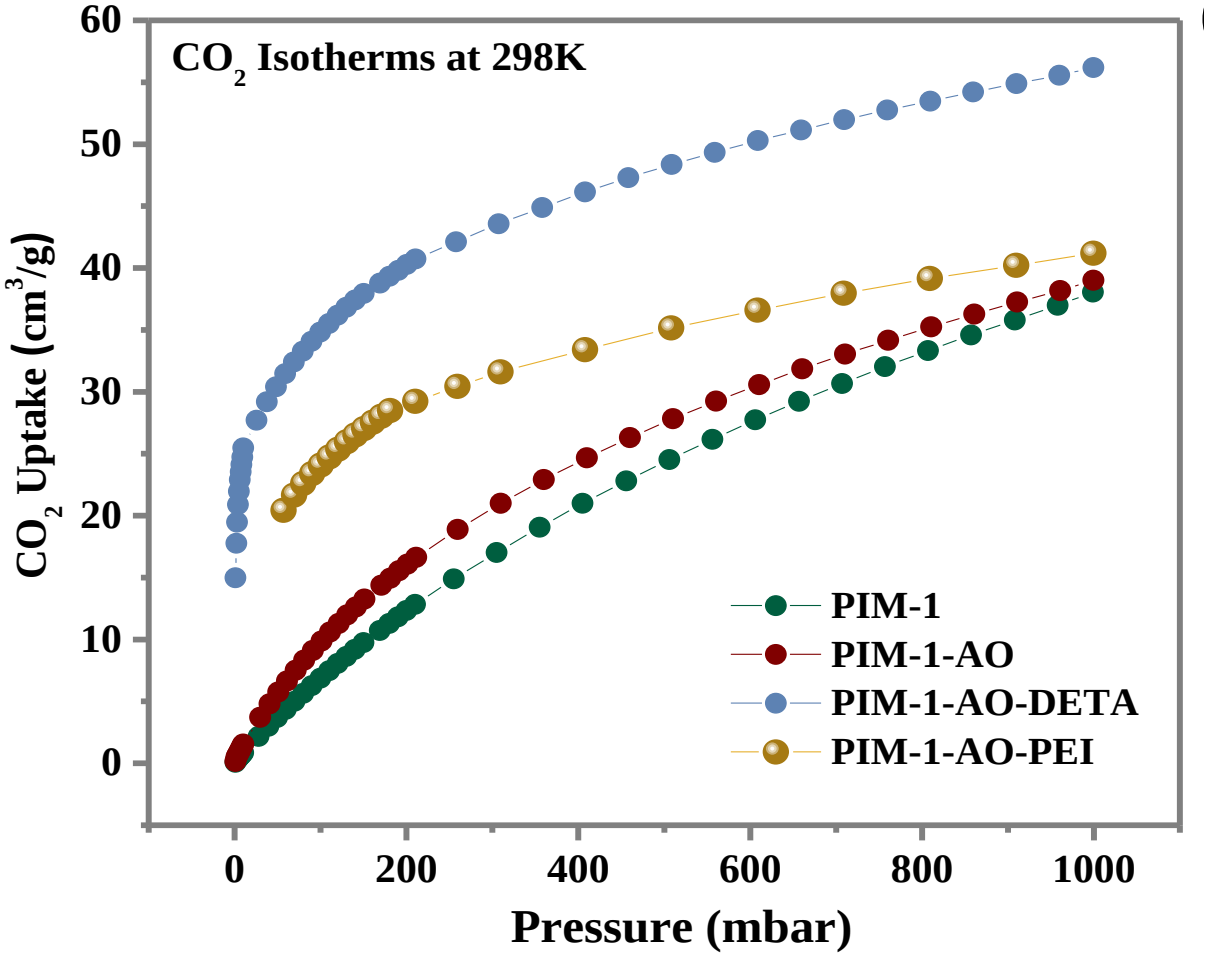
PIM -1-AO-DETA

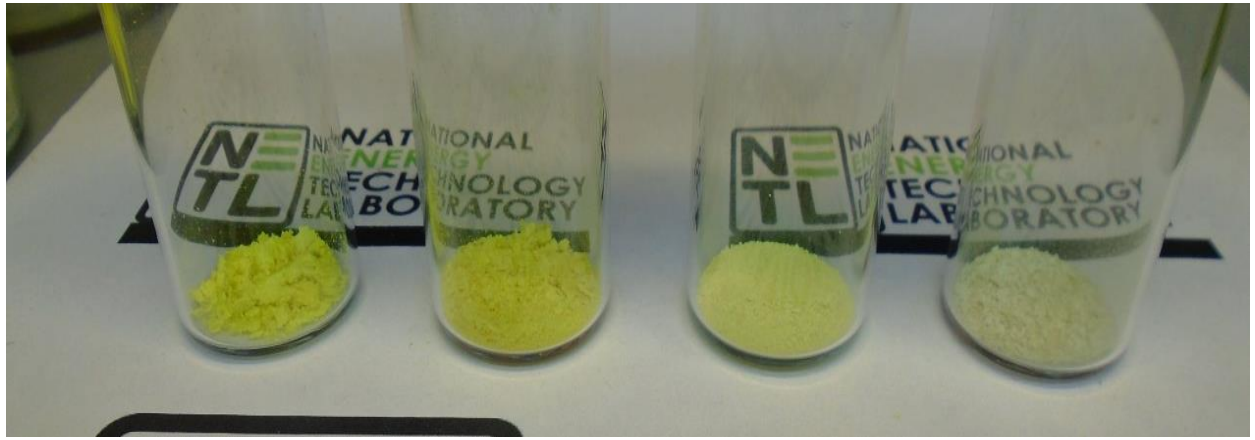
Amines considered:

- Diethylenetriamine (DETA)
- Tris(2 aminoethyl)amine (TAEA)
- Tetraethylenepentamine (TEPA)

Miles, A.; Wilfong, W. C.; Hopkinson D.; Sekizkardes, A. K. *Energy Technology*, **2020**, 8, 2000419

Amidoxime Functionalized PIM-1



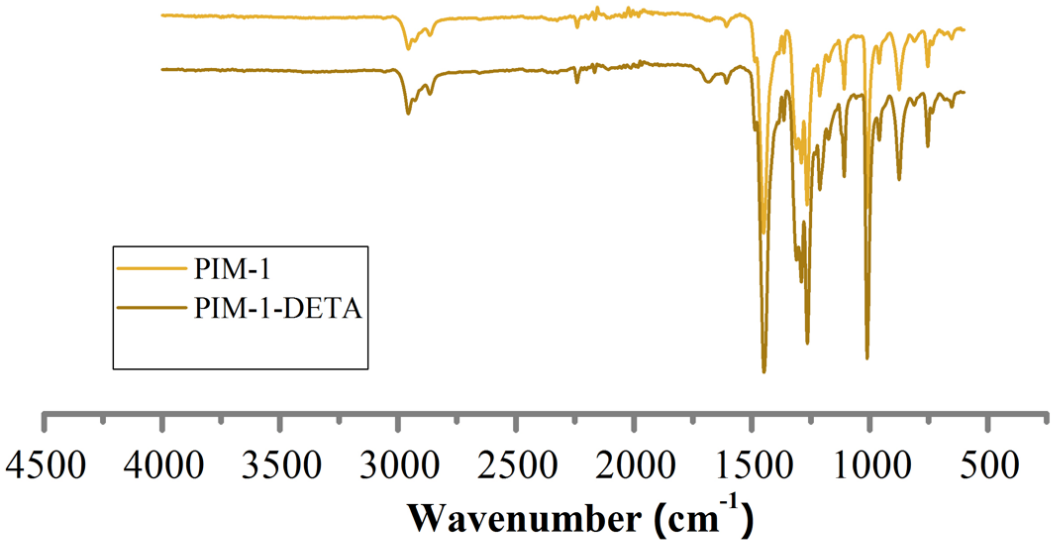


PIM-1 PIM-AO

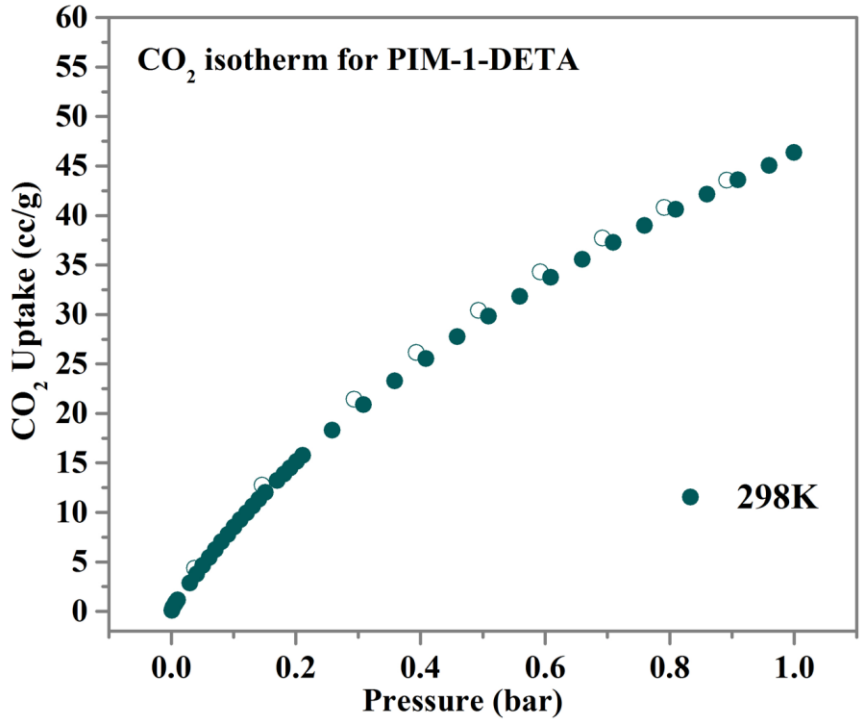
Miles, A.; Wilfong, W. C.; Hopkinson D.; Sekizkardes, A. K. *Energy Technology*, **2020**, 8, 2000419

Amine stability

- Control study with neat PIM-1

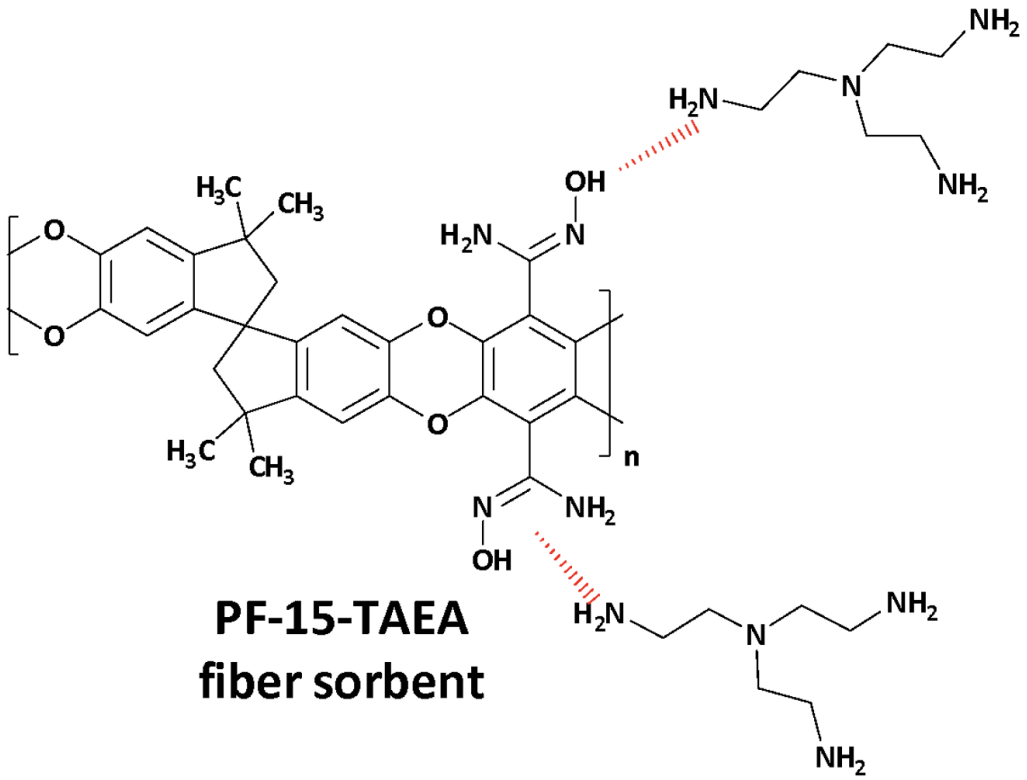


FT-IR spectrum of neat PIM-1 and PIM-1 -DETA (control sample)



PIM-1-AO Based Fiber Sorbent

PF-15-TAEA-fiber sorbent

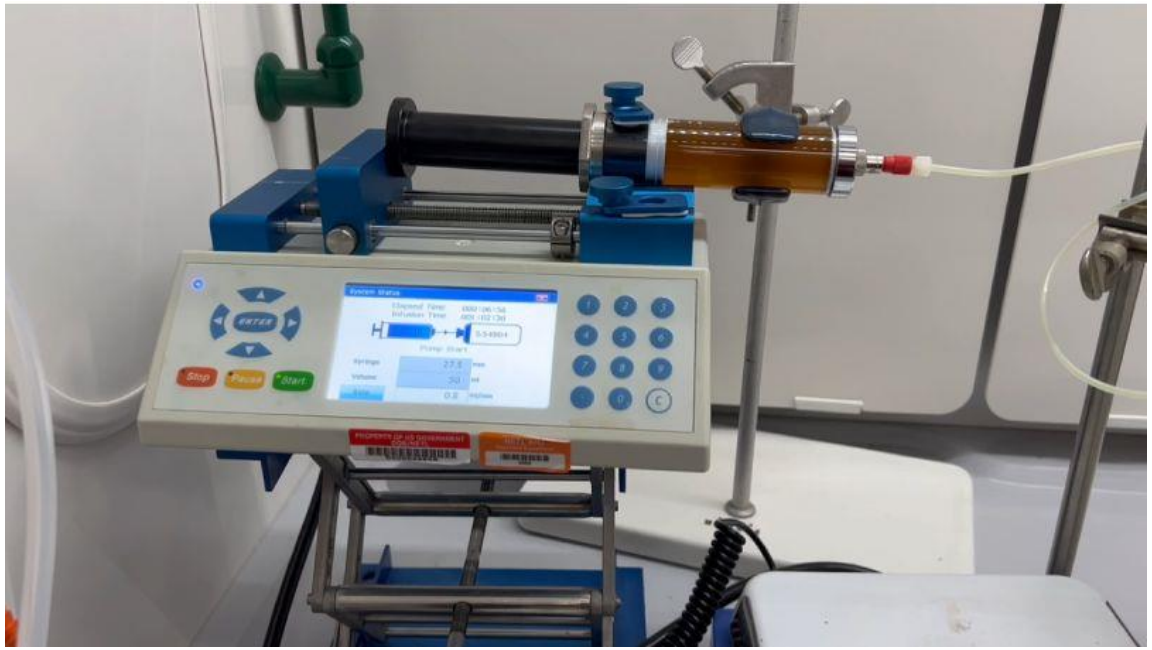


PF-15-TAEA fiber sorbent

- Fibers procced only from the sorbent formulation, no additives needed
- Cost-efficient synthesis and large-scale processibility
- High surface area substrate polymer
- Molecular amine use enabled by amidoxime functionality
- Amine loading is <25% in the sorbent

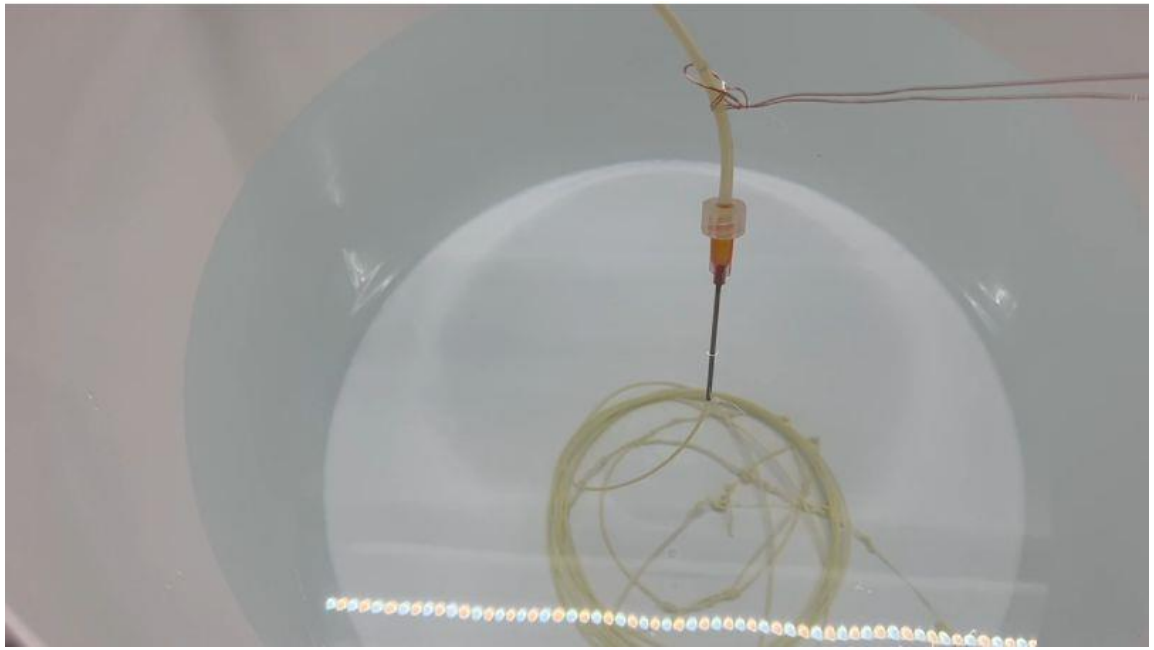
Sekizkardes, A. K. Kusuma V.; Culp J.; Muldoon P.; Steckel J.: Hopkinson D. *J. Mater. Chem. A*, **2023,** *11*, 11670-11674

Wet spinning of PF-15



Hopkinson D., Sekizkardes, A. K, Hoffman J., Yi S., Kusuma V. US Patent App. 17/891,153

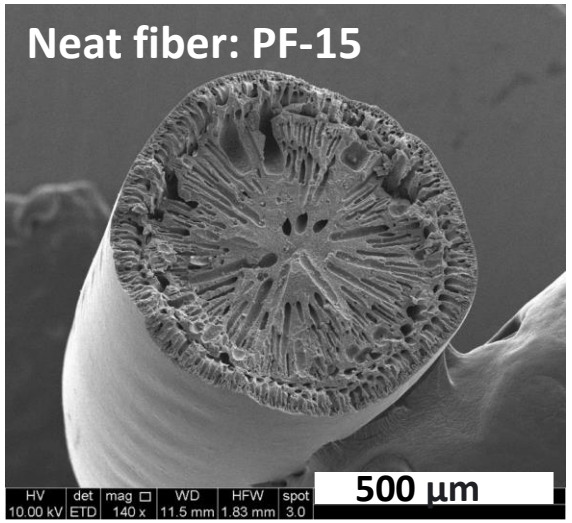
Wet spinning of PF-15

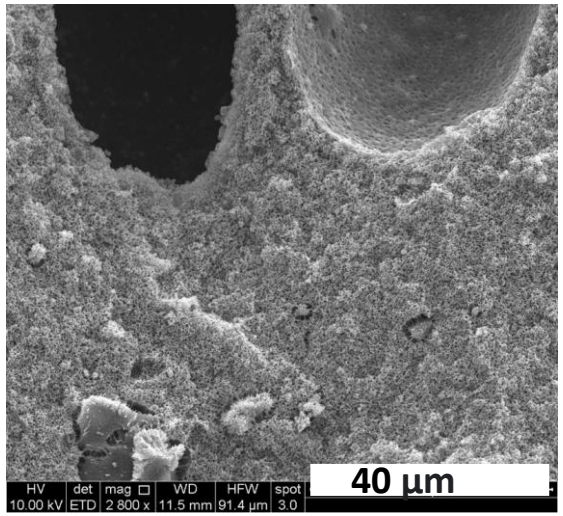


Hopkinson D., Sekizkardes, A. K, Hoffman J., Yi S., Kusuma V. US Patent App. 17/891,153

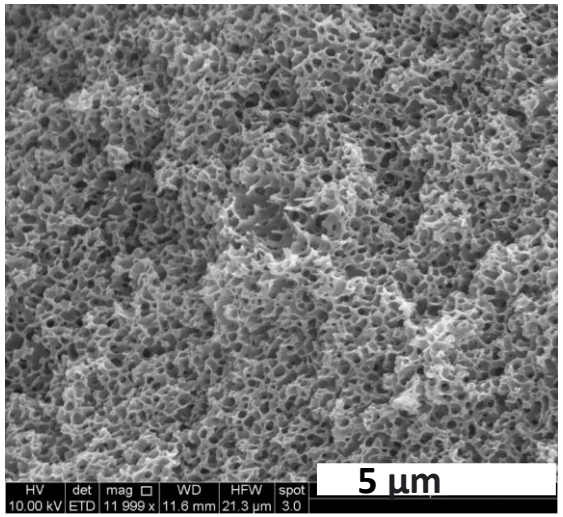
PF-15 fibers SEM

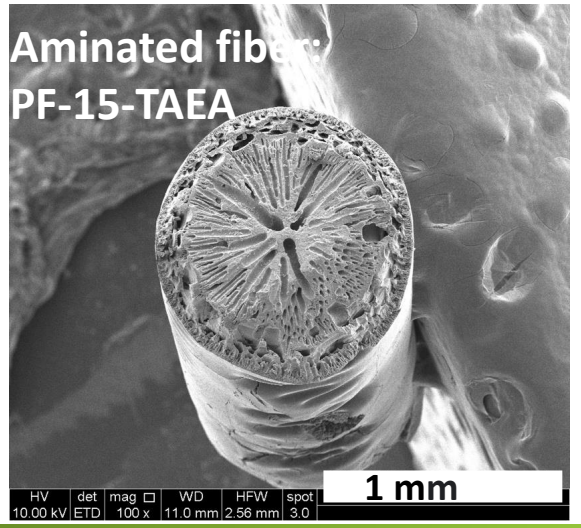
Internal surface (Cross-section)

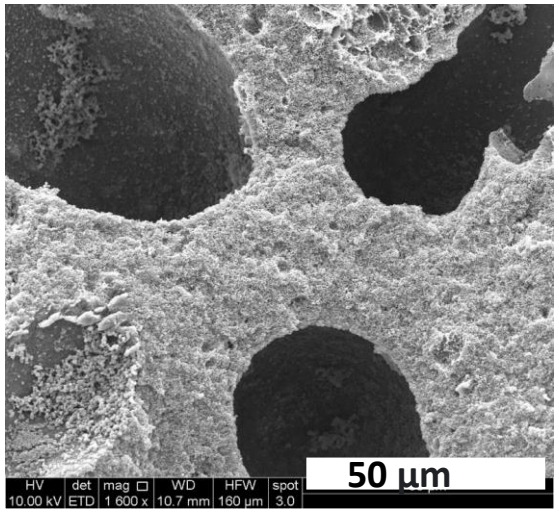


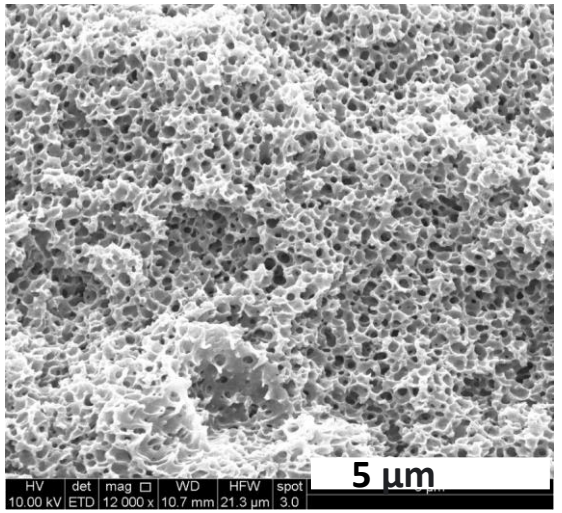


Internal surface (cross-section) magnified

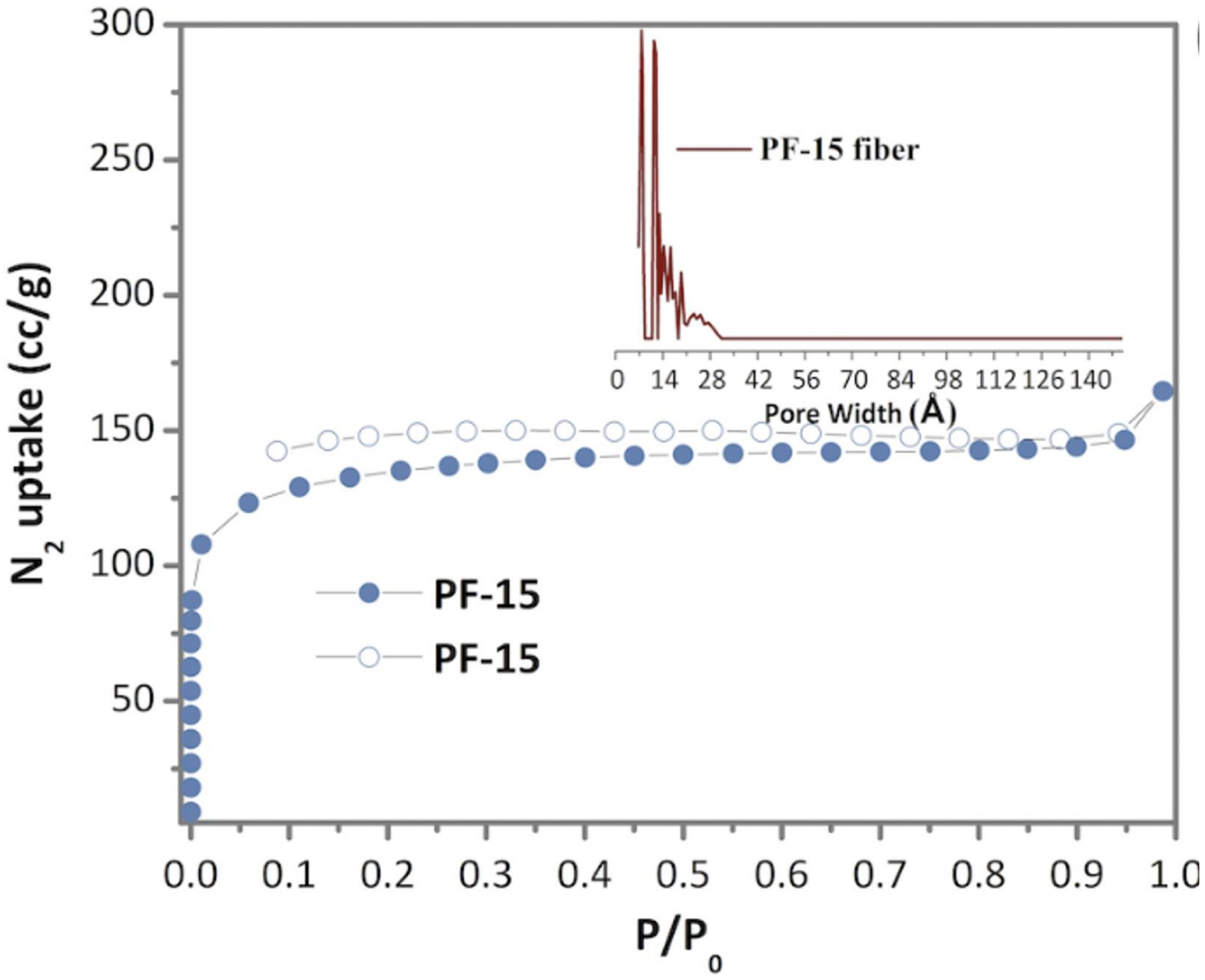


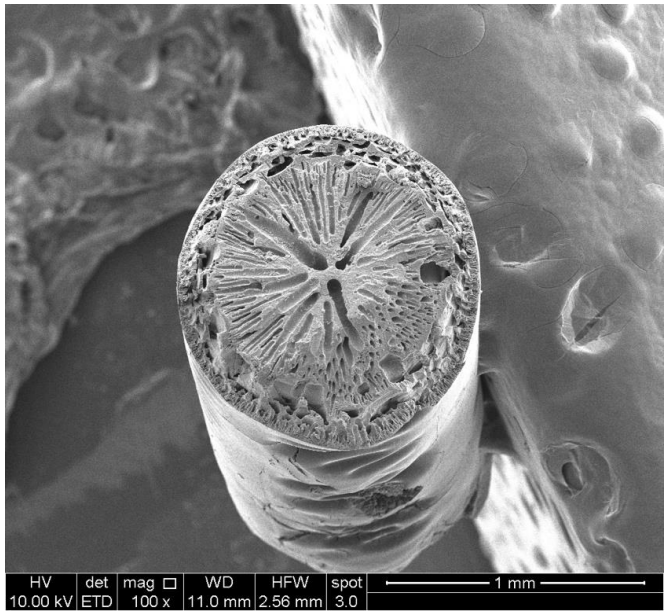




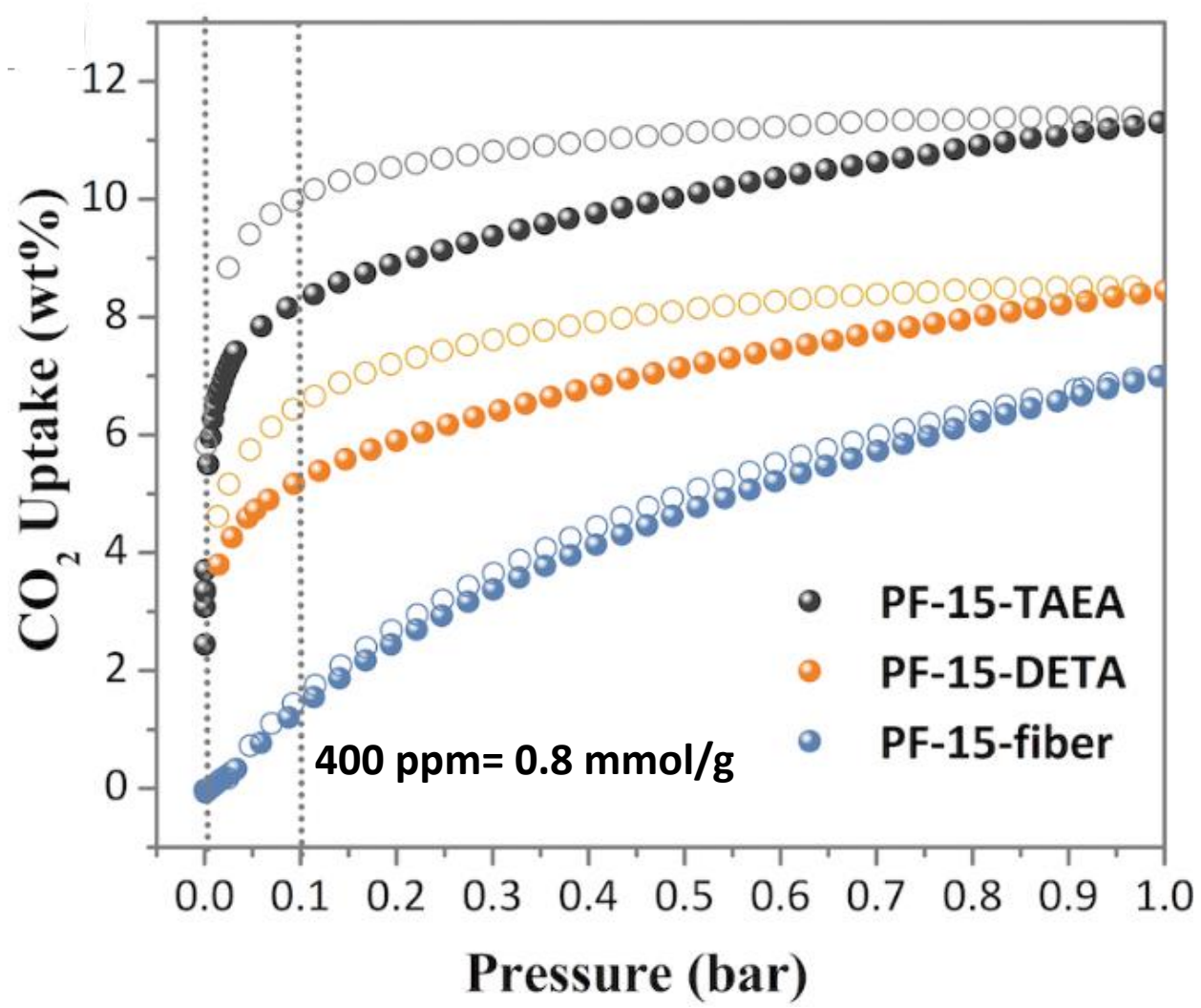


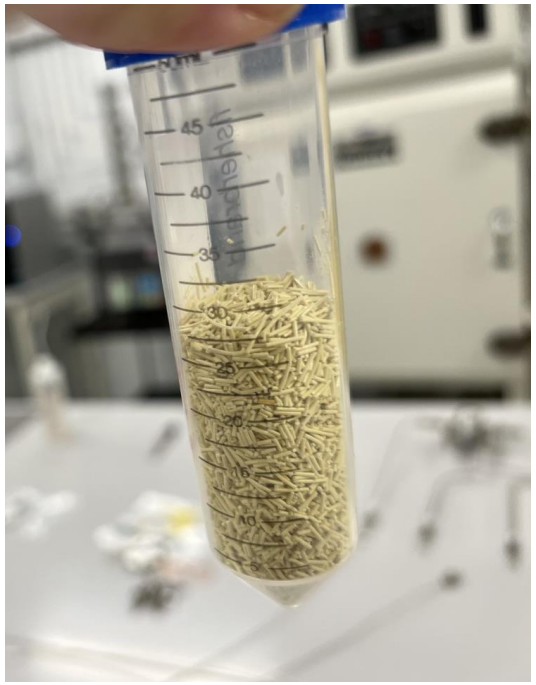
PF-15 fibers porosity



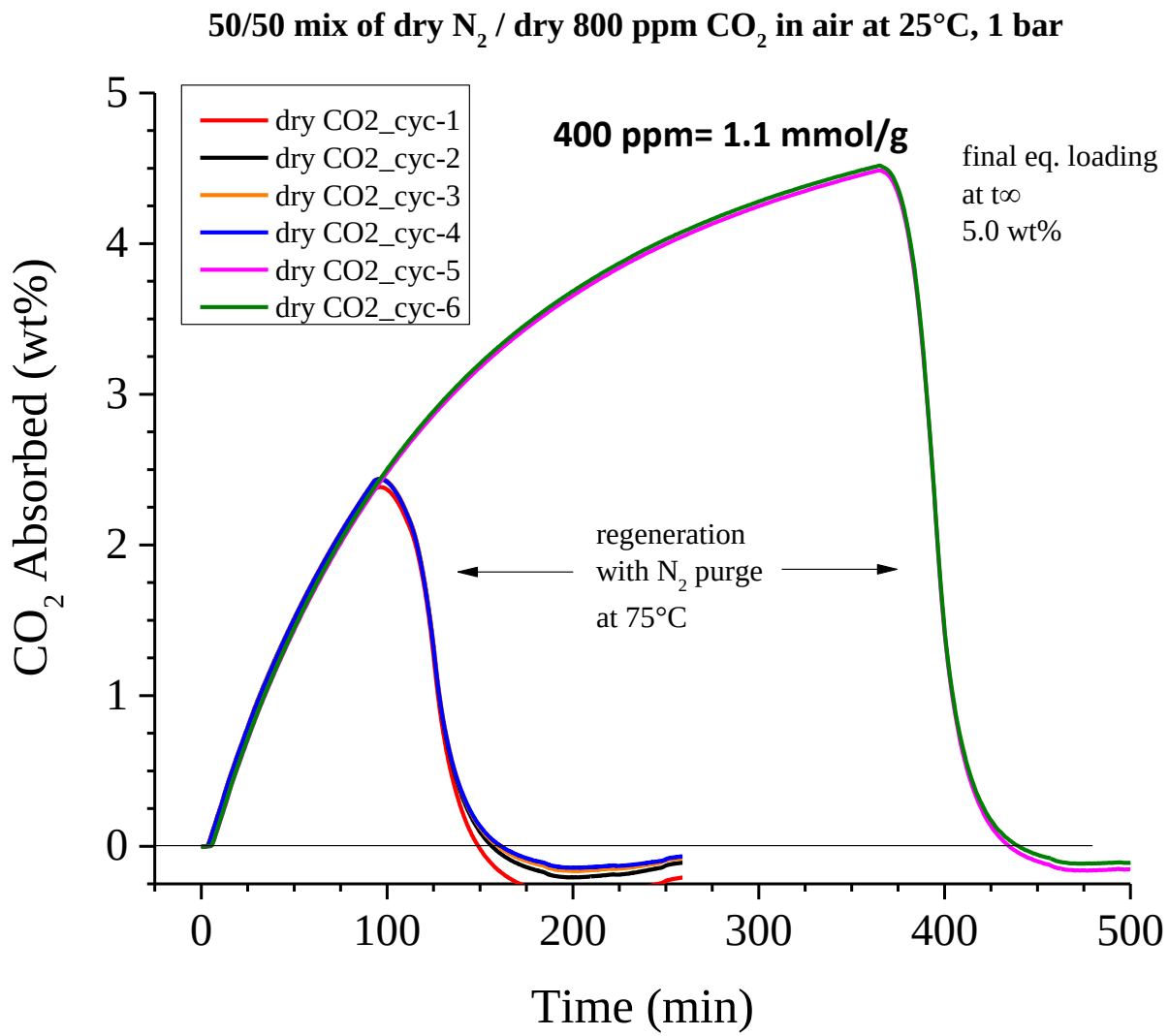


CO_2 Adsorption Test (Single Gas Volumetric)

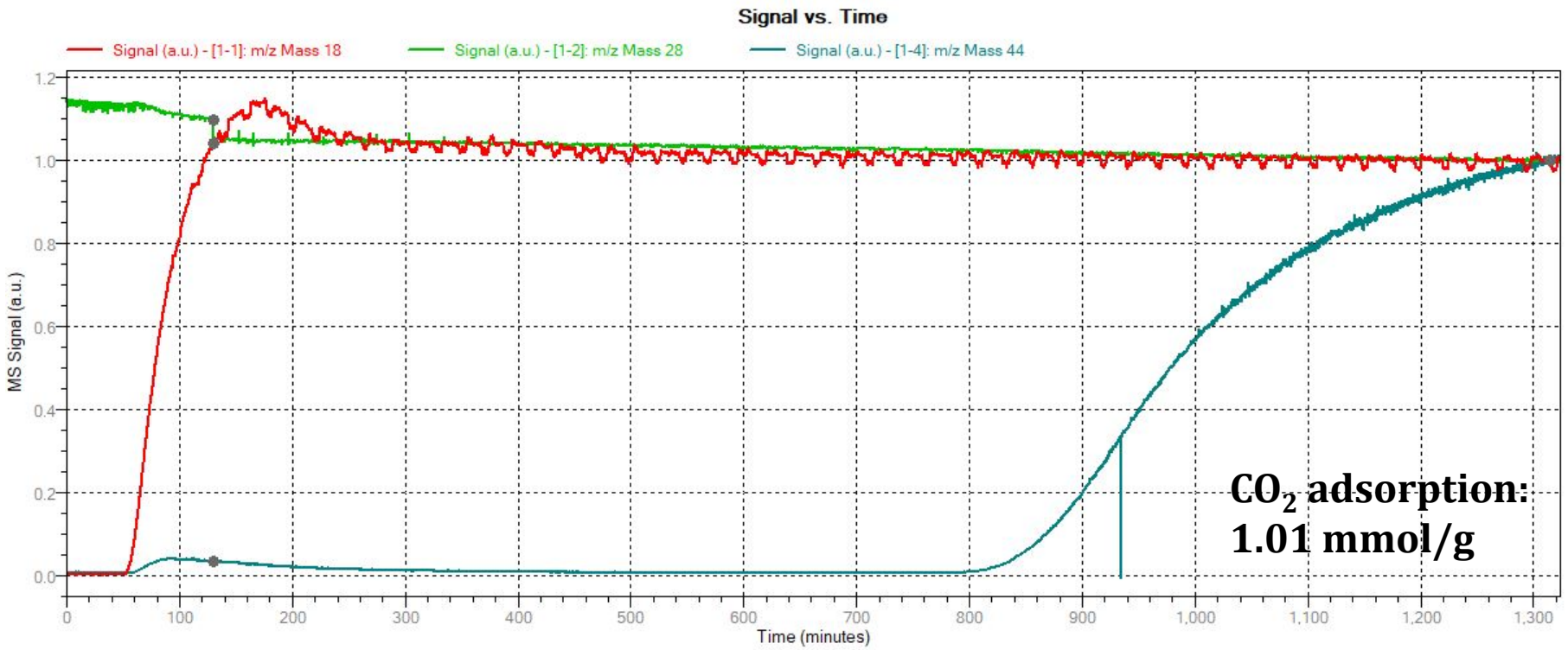




CO_2 Adsorption Test (Simulated Air Gravimetric)



Breakthrough analysis (Simulated Air RH 50%)

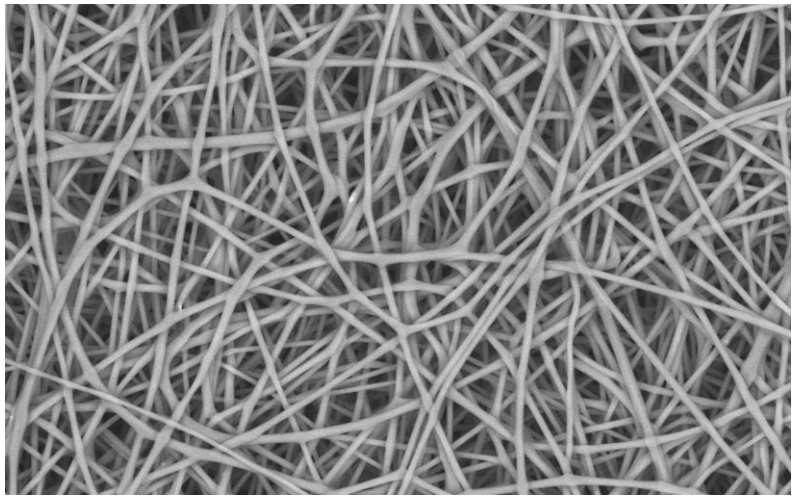


Breakthrough curves of H_2O (red), N2 (light green) and CO_2(blue) of the sorbent PF-15-TAEA under simulated wet air conditions: 400 ppm CO_2 concentration and 50 % RH at 25 C. The data was collected by Micromeritics Instrument Co.

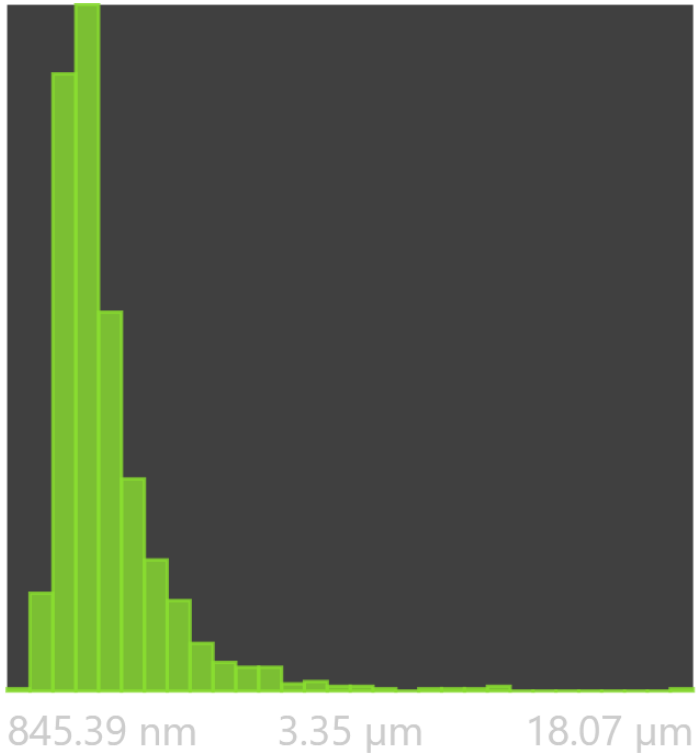
Other form factors:

Electrospun fibers

fibers: 30x5cm

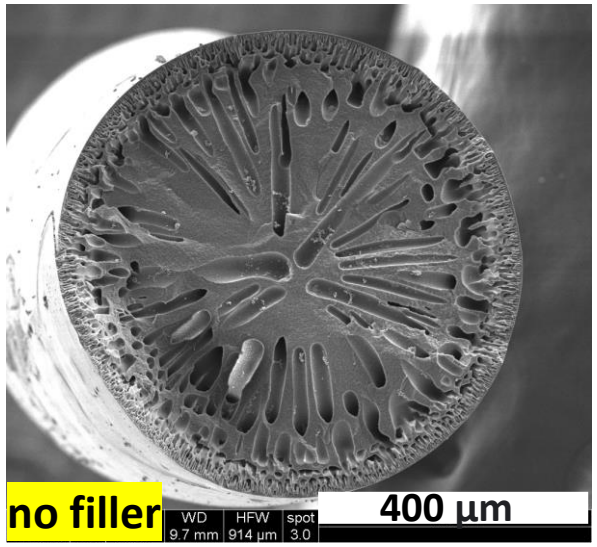


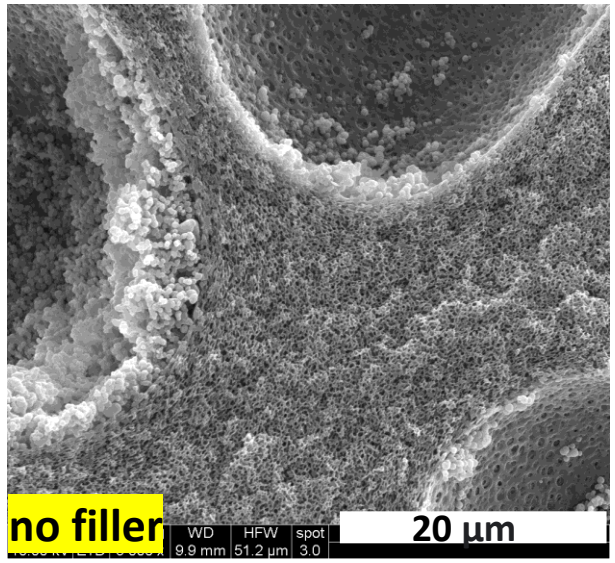
diameter of fibers: 2 micron

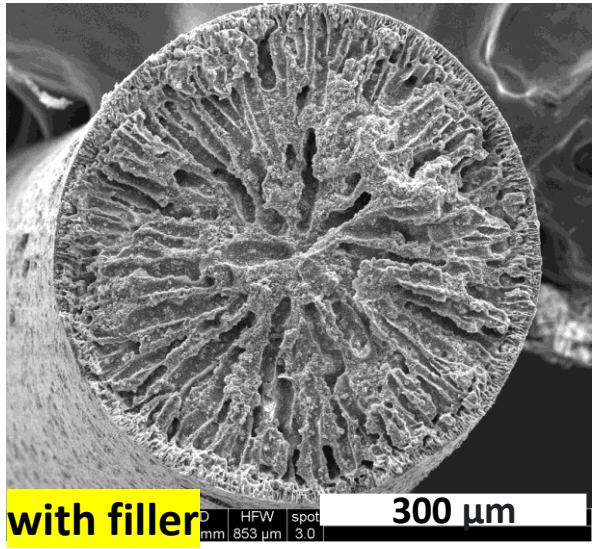


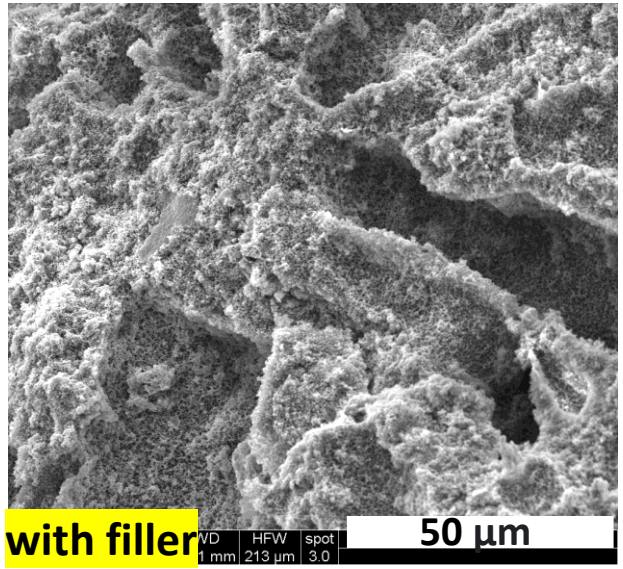
fiber diameter distribution

Filler incorporation in PF-15 fibers

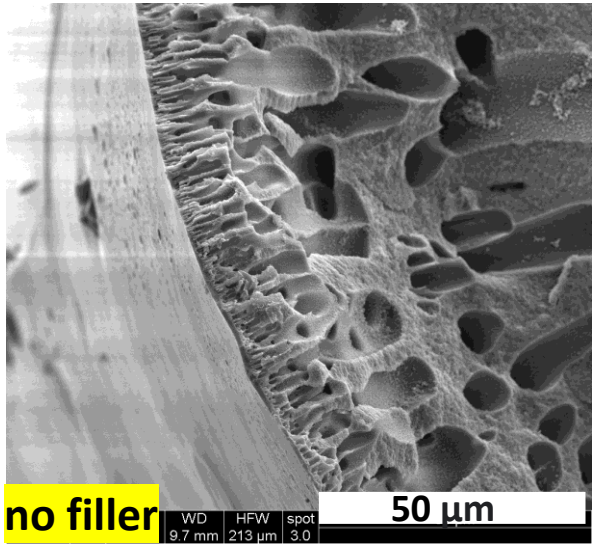


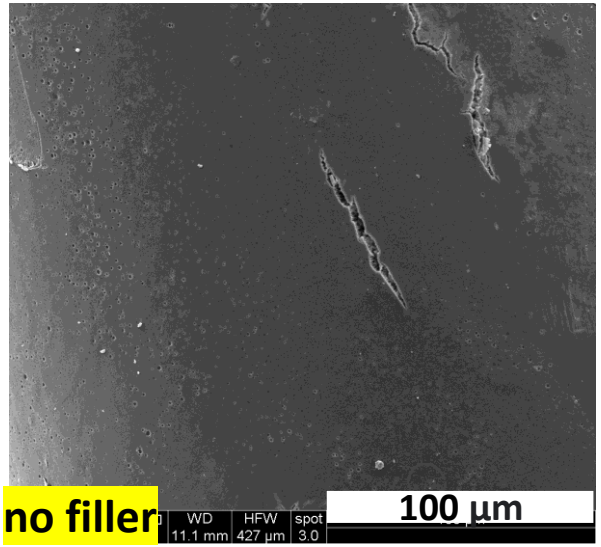


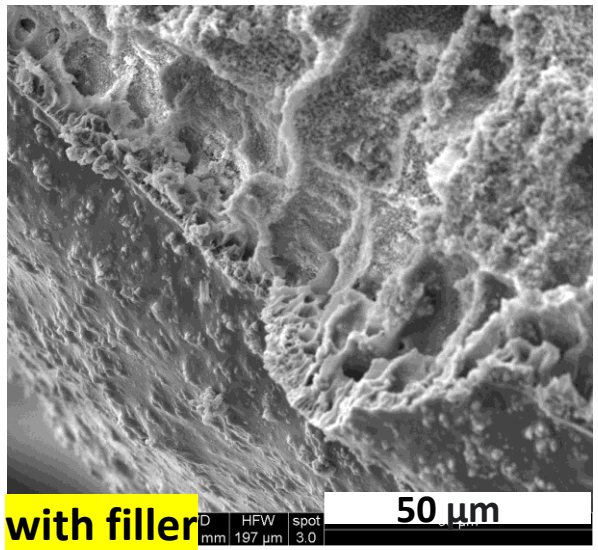


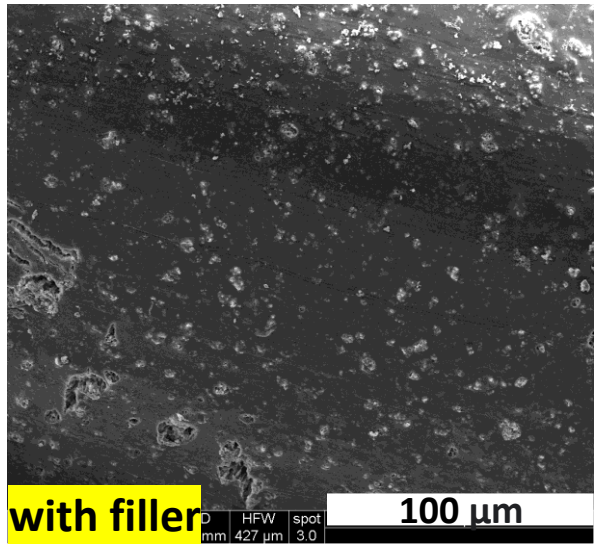


Filler incorporation in PF-15 fibers

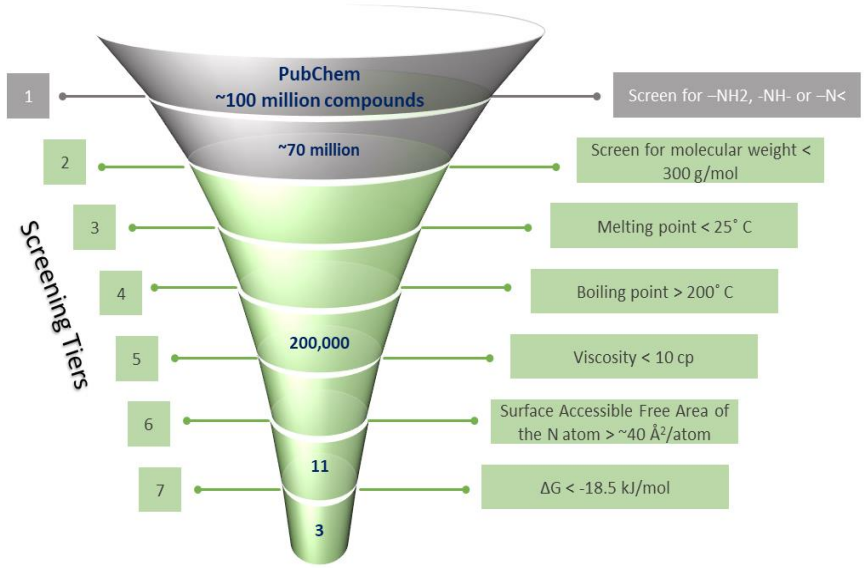




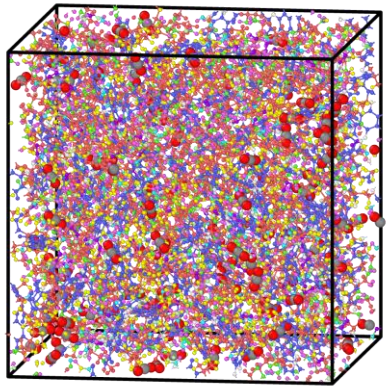




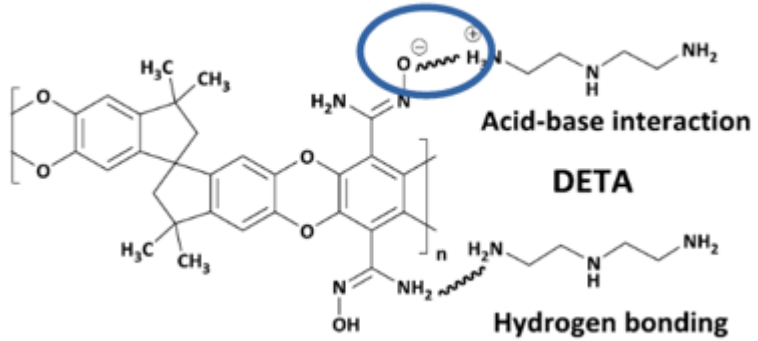
Computational Design of Alkylamine-Functionalized Polymer Sorbents

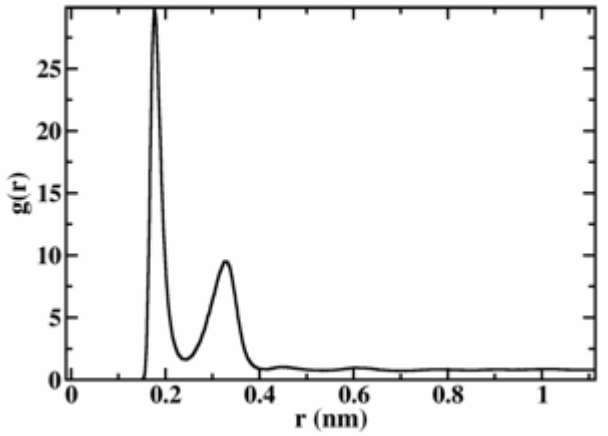


Screening of amines
(A final three amines exhibit more favorable CO2 reaction free energy and enthalpy than the existing TAEA amine)



An MD simulation box containing polymer, amine and CO2

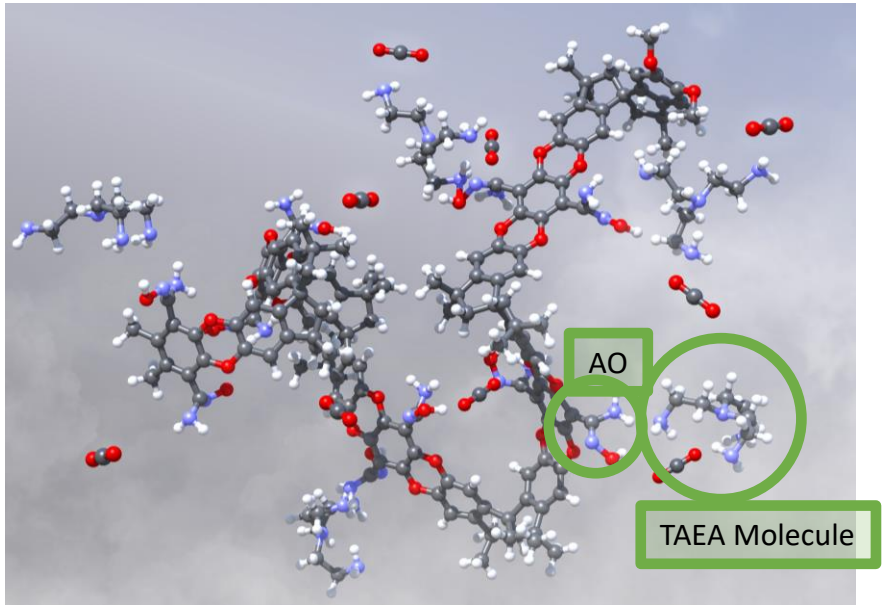




Molecular dynamics (MD) simulations are used for screening and to understand the adsorption mechanism

Summary and Outlook

- *Explore different sorbent formulation with the help of computational team.*
- *Monolith fiber scale up*
- *Electrospun fiber production*
- *Flat sheet fiber production*
- *Testing the sorbents under simulated DAC conditions*
- *Exploring the filler candidates to be used in the polymer*



PIM-1-AO backbone has:

- Stiff, straight sections that consist of fused rings (ladder polymer)
- Sharp kinks caused by the spiro center

Gray = carbon
Red = oxygen
White = hydrogen
Blue = nitrogen1

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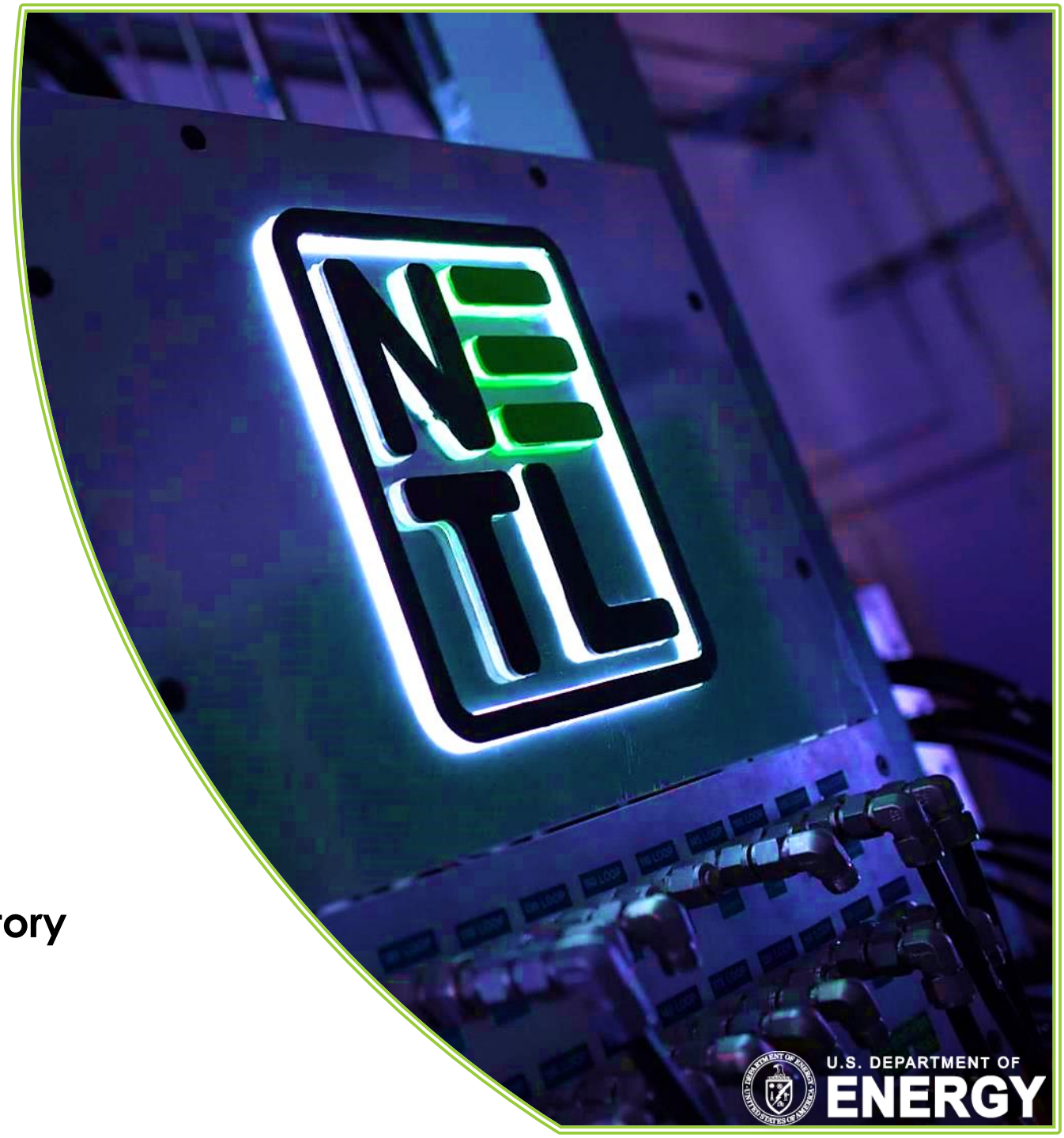

Thank You