Mixed Matrix Membranes for Post-Combustion Capture

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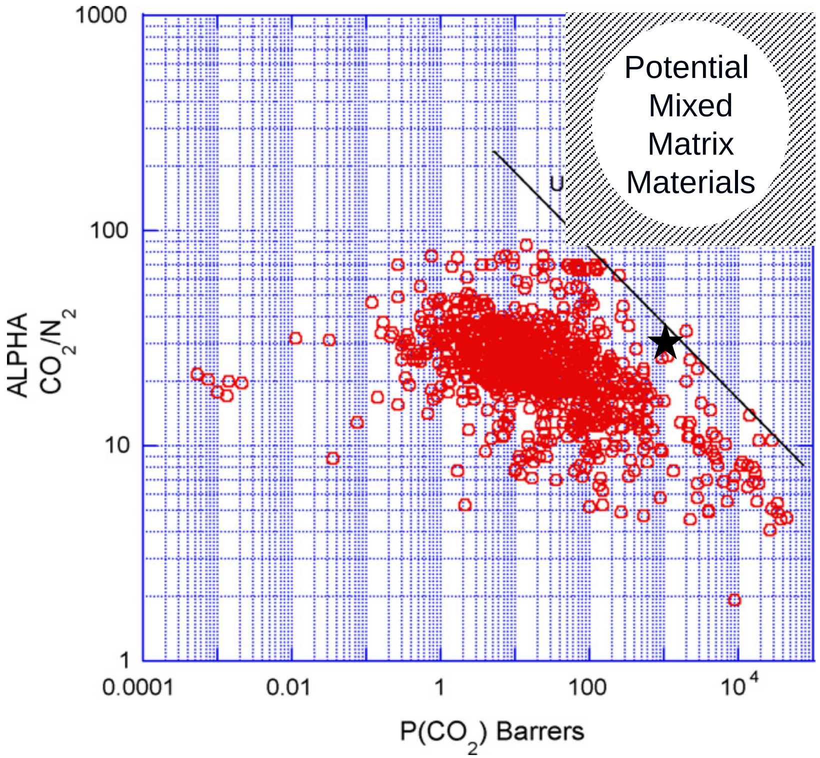
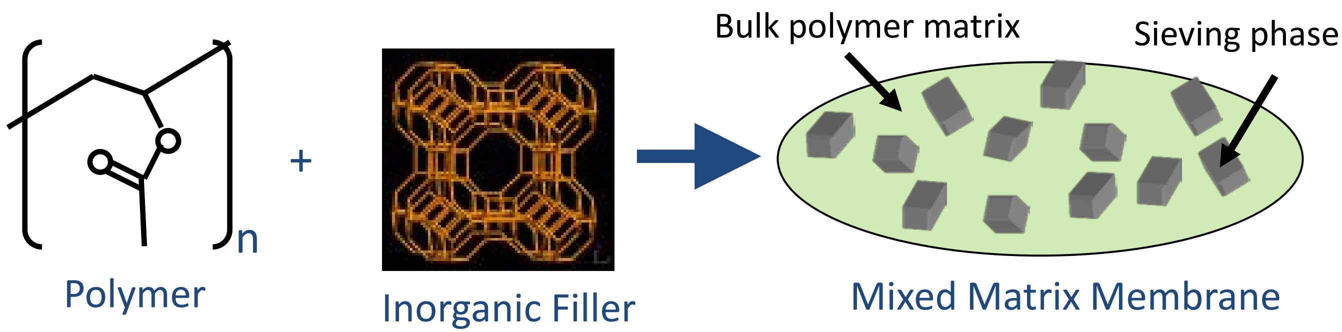
Carbon Capture Technology Meeting

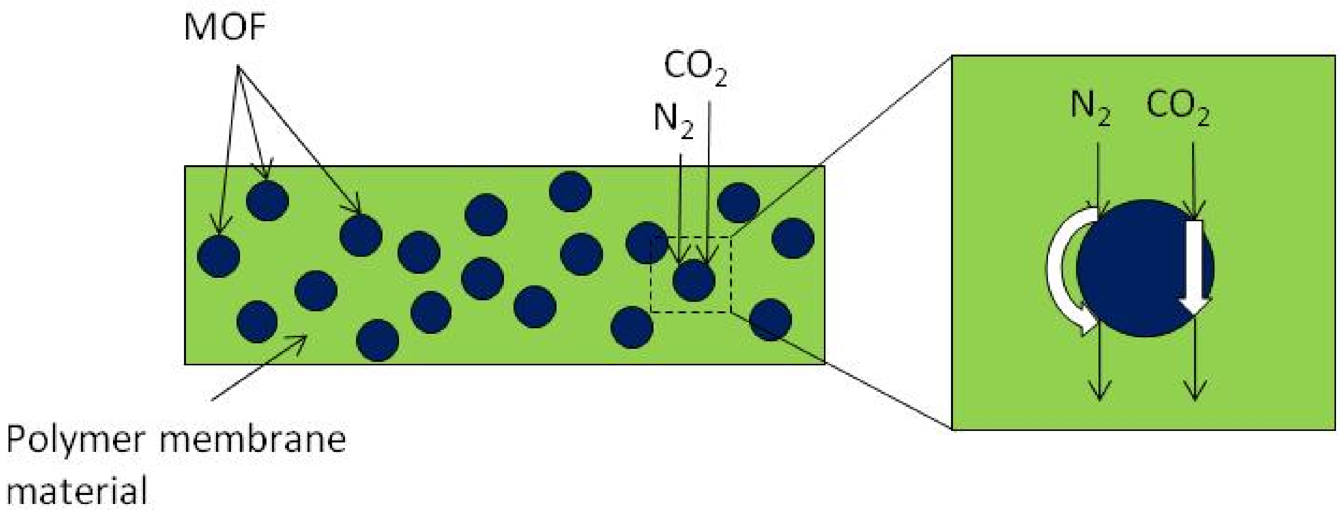
Mixed Matrix Membranes

- **Trade-off exists between permeability and selectivity for the pure polymers**
- **MMMs have the potential to exceed the Robeson upper bound**
- **Combine the processability of polymer with superior gas separation of filler (sieves)**





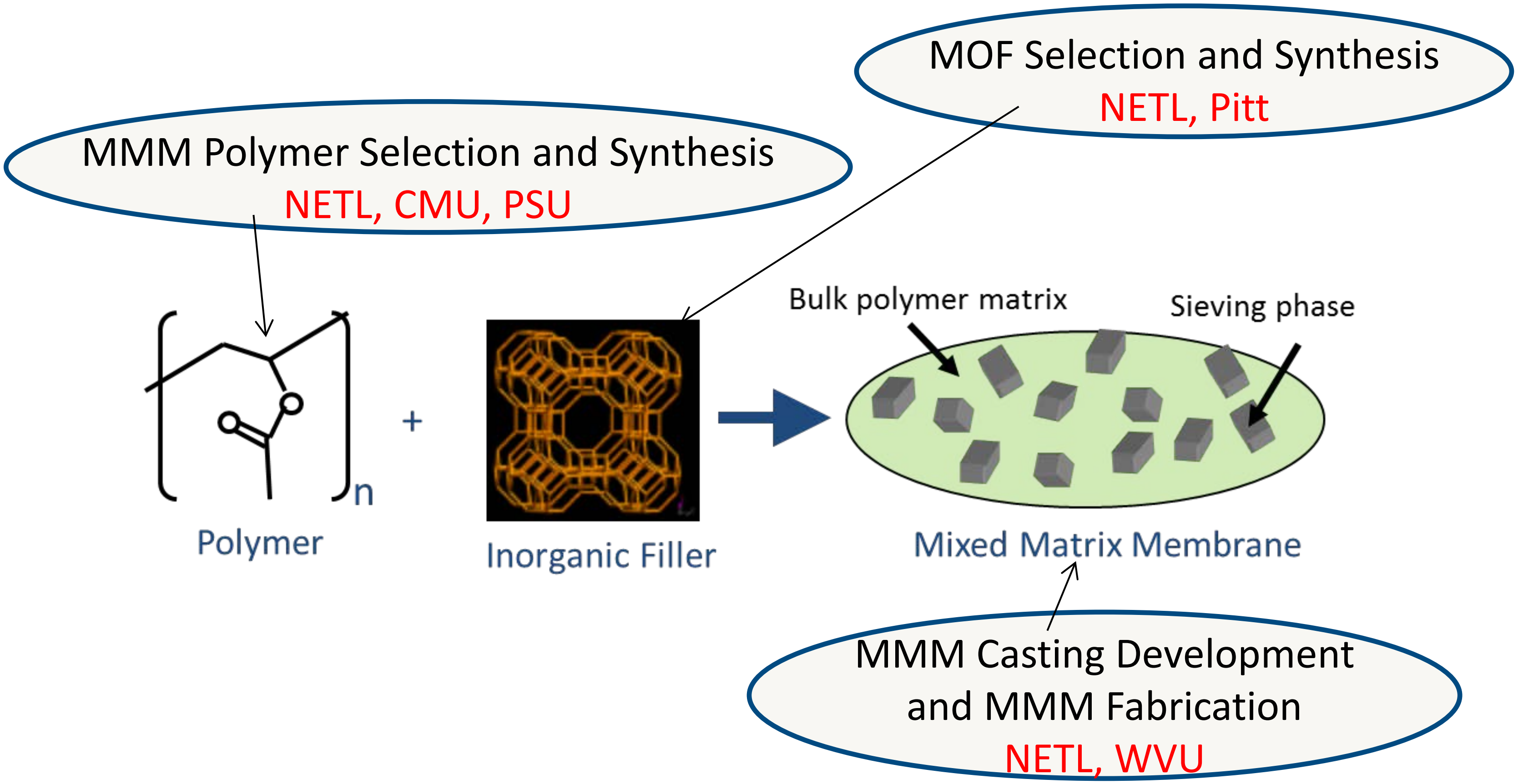
MOF-based Mixed Matrix Membranes



CO_2 diffuses through MOF quickly; N_2 takes slower path around particle

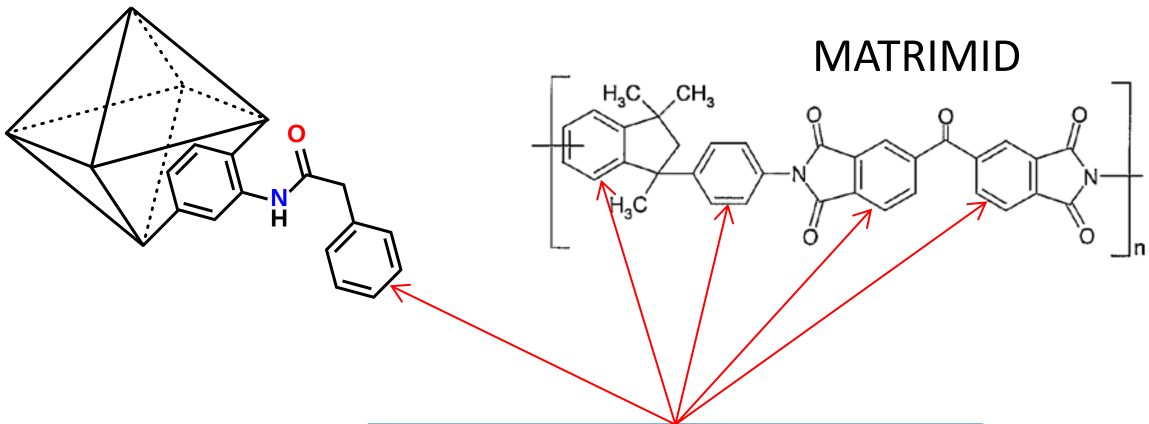
- **MOF filler particles in a polymer matrix**
  - MOF Particles have shown promise as a CO_2 sorbent and the pore size can be tuned based on the linker.
- **The goal is to achieve separation properties like those of the filler rather than the polymer.**
- **Polymer membrane fabrication is potentially 10-fold less expensive than fabrication of membranes from crystalline materials like MOFs.**

Approach


MOF Selection and Synthesis
NETL, Pitt
MMM Polymer Selection and Synthesis
NETL, CMU, PSU
Bulk polymer matrix
Sieving phase
n
+
Polymer
Inorganic Filler
Mixed Matrix Membrane
MMM Casting Development
and MMM Fabrication
NETL, WVU

Previous work at NETL

- **Development of a technique to overcome the defects at the polymer/filler interface**



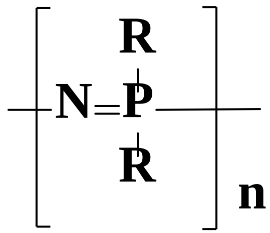
Aromatic structures should provide for good interaction!

Current Work

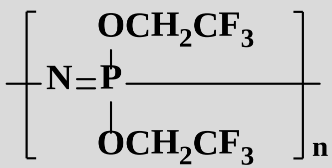
Two polymer/MOF systems being investigated

- Polyphosphazene/SIFSIX
- Cerenol/UiO-66

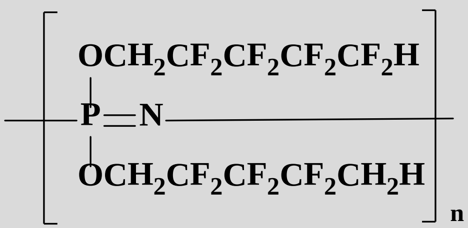
Polyphosphazenes



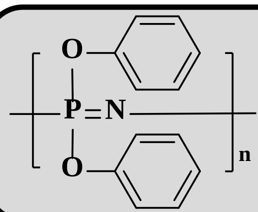
- Inorganic polymer
- High permeability
- Good film formation
- Tunable through ‘R’ group



Poly[bis(trifluoroethoxy)phosphazene] (TFE)



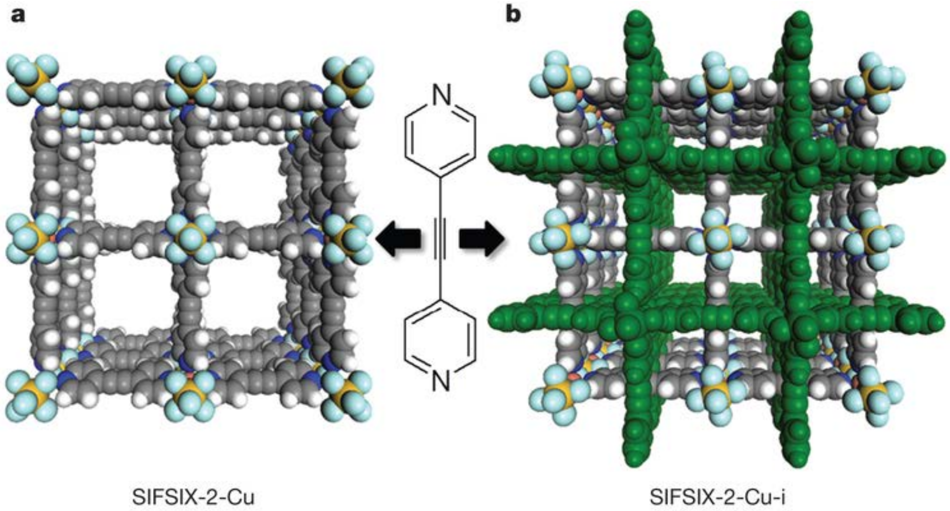
Poly[bis(octafluoropentoxy)phosphazene] (OFP)



Poly[bis(phenoxy)phosphazene] (PHP)

SIFSIX

- System does not adsorb water
- High CO_2 solubility selectivity over N_2
- Fluorinated groups should provide good interaction
- Pore size ~5Å



Nugent, P. et. al. *Nature.* **2013.** *495*, 80.

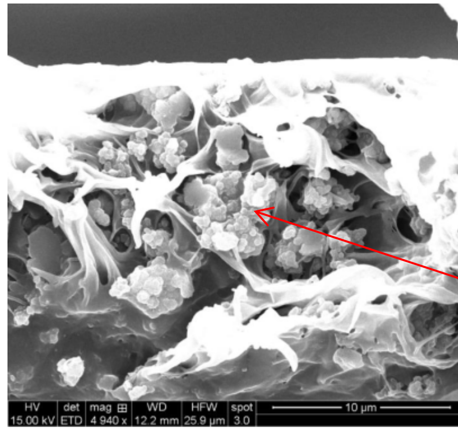
Polyphosphazene Films

Polymer	CO_2 Permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
Phosphazene-TFE	317 ± 9	27 ± 2	14 ± 1
Phosphazene-OFP	1270	670	1.9
Phosphazene-PHP	4.6 ± 0.2	1.3 ± 0.1	3.3 ± 0.2

Phosphazene-TFE selected for MMM fabrication

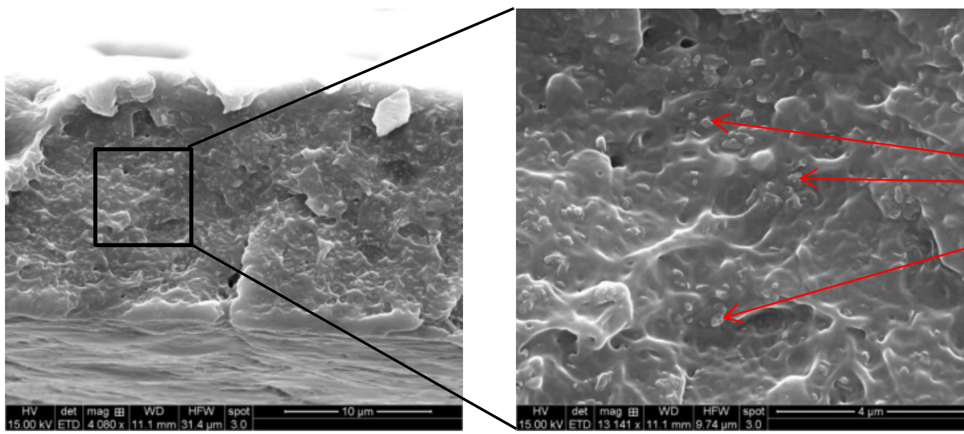
Polyphosphazene MMMs

TFE/UiO-66-NH2
MMM cross-section



MOF w/
poor adhesion &
agglomeration

TFE/SIFSIX MMM
cross-section



MOF

SEM images show ‘good’ adhesion between polymer and MOF for SIFSIX filler

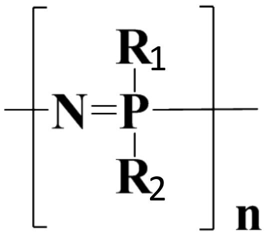
Polyphosphazene MMM Separation Performance

Phosphazene Membrane	MOF	Loading	CO_2 Permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
Neat TFE	NA	NA	317 ± 9	27 ± 2	14 ± 1
TFE MMM	UiO-66-NH2	10 wt%	354 ± 8	34 ± 4	11 ± 1
TFE MMM	UiO-66-NH2	23 wt%	314 ± 14	40 ± 5	8 ± 1
TFE MMM	SIFSIX	10 wt%	360 ± 6	22 ± 1	17 ± 1

Improved performance observed for TFE/SIFSIX combination
BEST OPTION FOR HOLLOW FIBERS

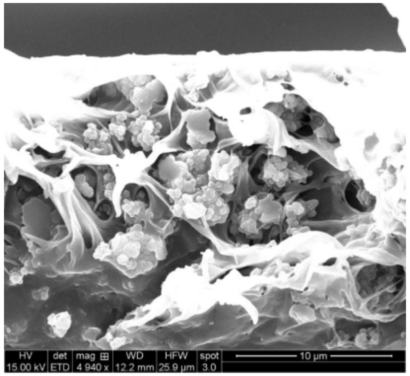
Moving Forward - Polyphosphazene

- **Different side chains**



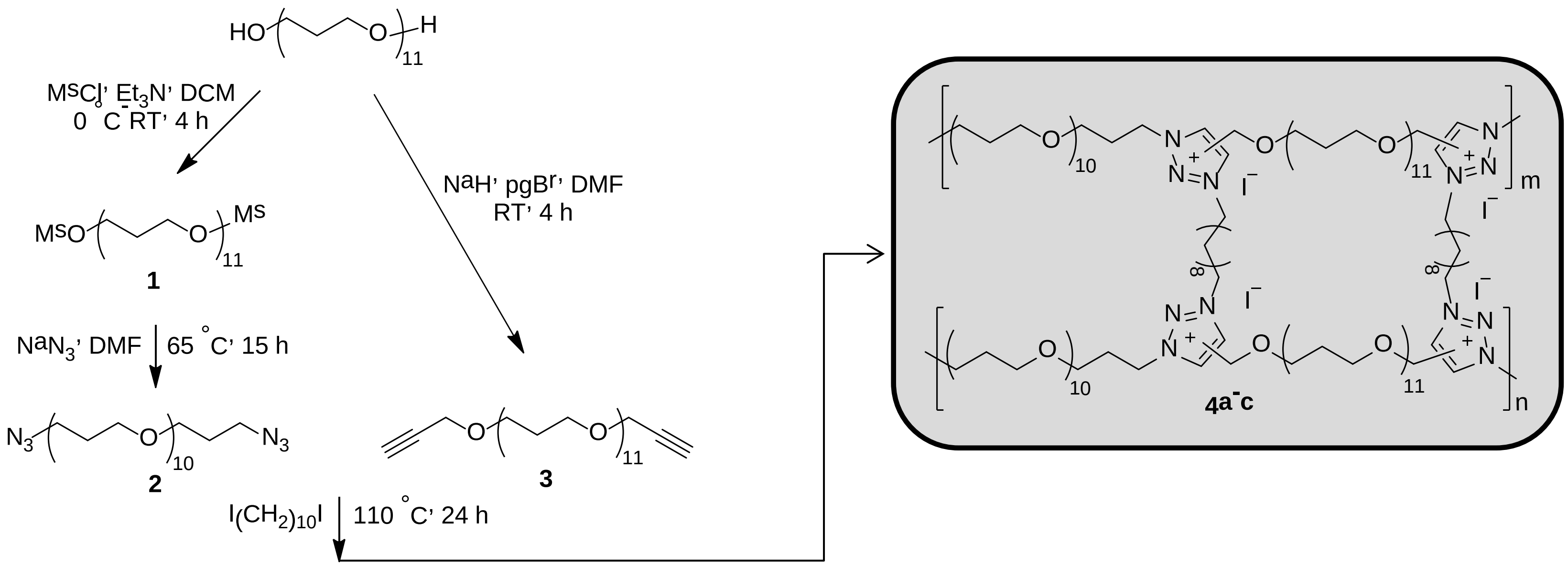
$R_1 \neq R_2$

- **Surface functionalization of Gen 1 MOF for improved adhesion**



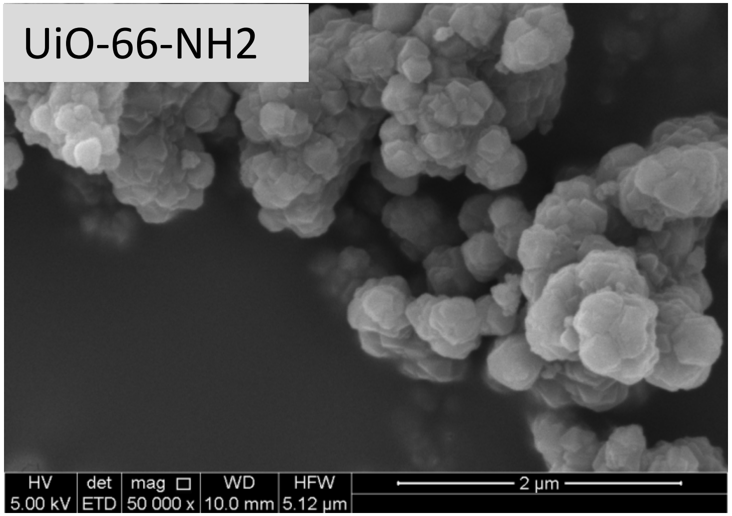
- **Continue hollow fiber development and testing**
  - Simulated flue gas stream including moisture and contaminants

Cerenol

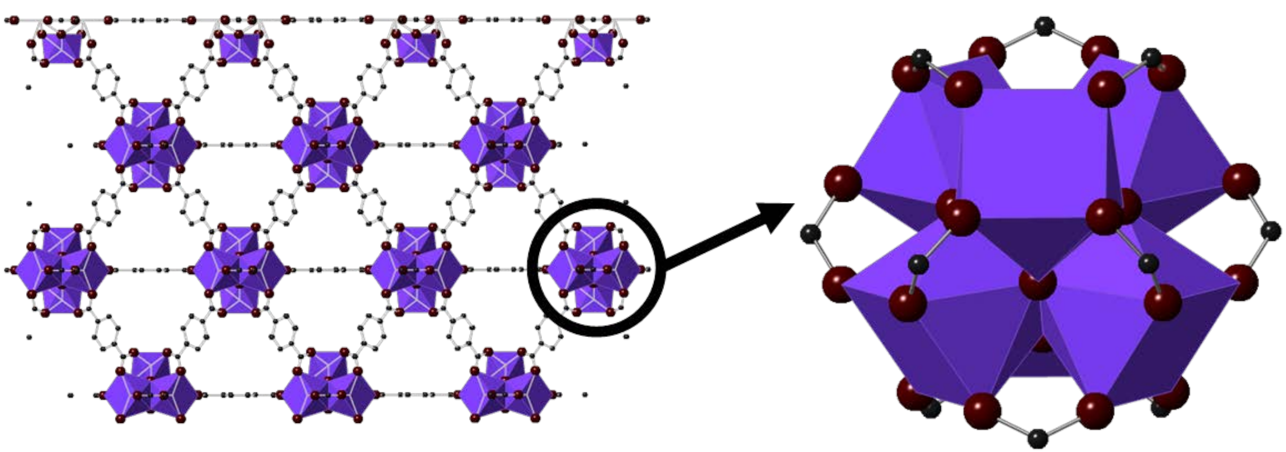


- Ether groups for CO_2 interaction
- Ionic character for CO_2 interaction
- Crosslinking for structural properties
- Tunable – many 'knobs to turn'
- Two different basic formulations

UiO-66-NH2



- Good CO_2 uptake
- Stable in the presence of water
- Can be surface functionalized through the linker



Cerenol Films

Polymer	Crosslinker loading	CO_2 Permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
Cerenol-650	12 wt%	113 ± 4	6.0 ± 0.3	19 ± 1
Cerenol-650	22 wt%	86 ± 2	2.1 ± 0.0	41 ± 1
Cerenol-650	36 wt%	97 ± 3	2.7 ± 0.1	37 ± 1

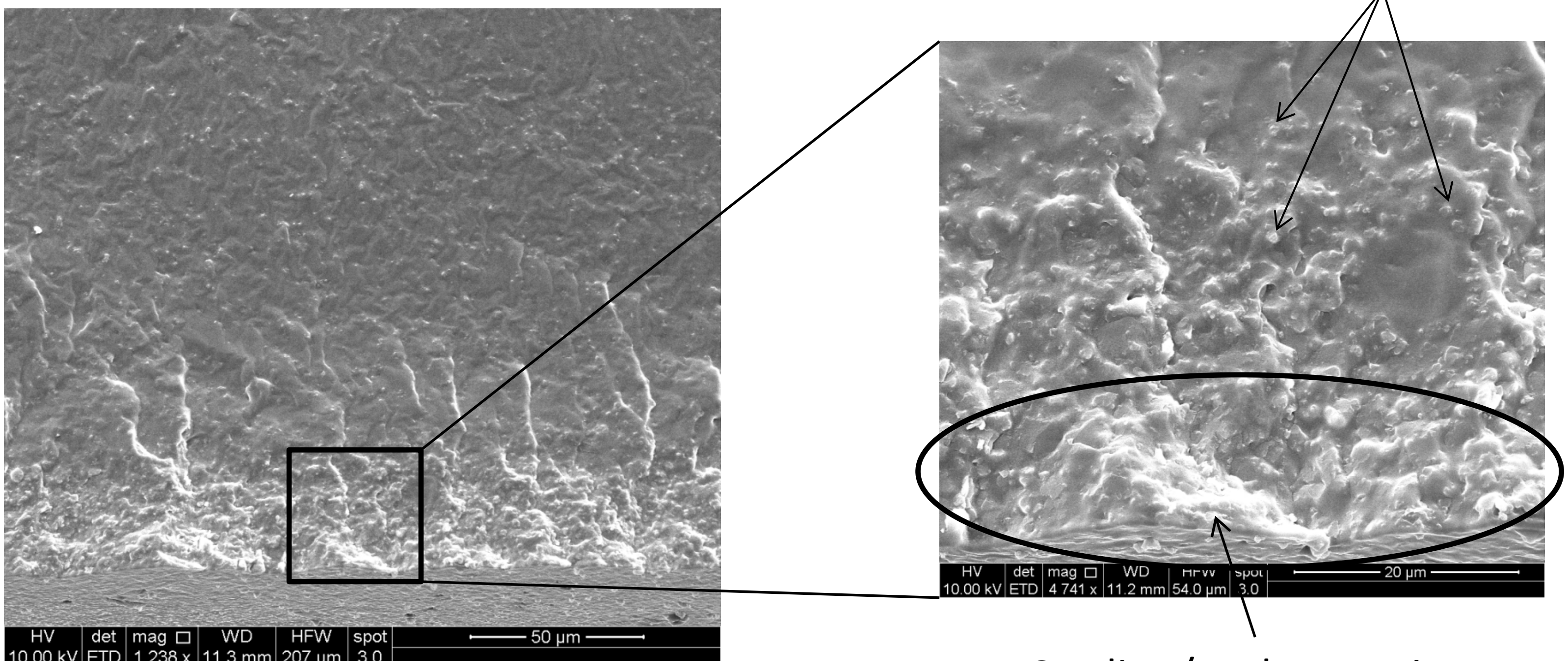
- Good permeability and good selectivity
- Minimum of 22 wt% crosslinker yields best results
- Take advantage of ether character for good MOF adhesion?

Excellent potential as a MMM material

Cerenol MMMs

Cerenol/UiO-66-NH2 MMM

MOF

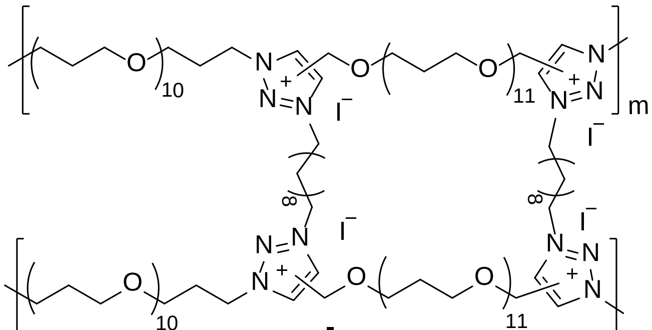


Settling/agglomeration

SEM images show potential for 'good' adhesion but also show settling – efforts underway to address this issue

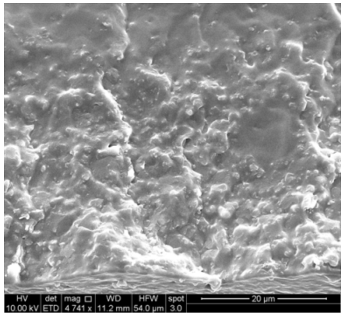
Moving Forward - Cerenol

- **Optimize variables**
  - Crosslinker length
  - Anion



4a⁻c

- **Resolve settling of MOF**
  - Increase viscosity of polymer dope



- **Continue hollow fiber development and testing**
  - Simulated flue gas stream including moisture and contaminants

Improvement Compared to Previous Work at NETL

	Previous Work at NETL	Polyphos./ SIFSIX	Cerenol	Cerenol/ UiO-66
Permeability	<30 Barrer	**360**	**97**	**Potential for 100+**
Selectivity	30-40	17	**37**	**Potential for 40+**
Potential for improvement	minimal	**yes**	**yes**	**yes**

Summary

- **2 MMM systems under development**
- **Phosphazene-TFE/SIFSIX MMM successfully fabricated**
  - Permeability of 360 Barrer
  - Selectivity of 17
- **Cerenol films fabricated**
  - Permeabilities of 86-113 Barrer
  - Selectivities of 19-41
  - Best combination: Permeability = 97, Selectivity = 37
- **MMM Hollow Fibers in development for contaminant and moisture testing**

Acknowledgements/Disclaimer

- **Polyphosphazene development**
  - Prof. Allcock, Zhicheng Tian, Andrew Hess
- **Cerenol development**
  - Hunaid Nulwala, Xu Zhou
- **MOF development**
  - Prof. Rosi, Alex Spore, Tao Li, Santosh Kumar
- **Membrane fabrication and testing**
  - Surendar Venna, Shan Wickramanayake
- **Carbon Capture Group Lead**
  - Dave Luebke

Questions???