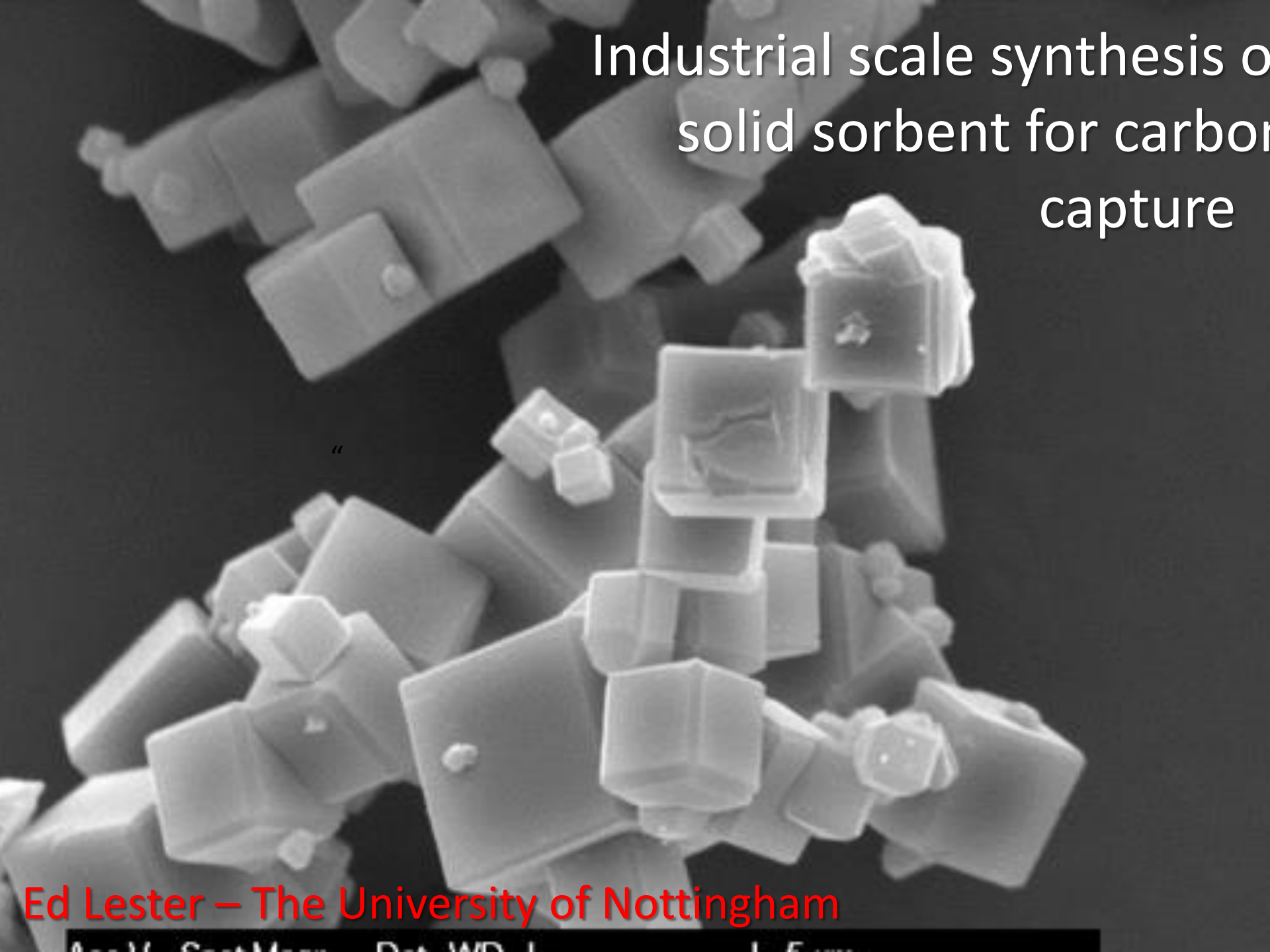
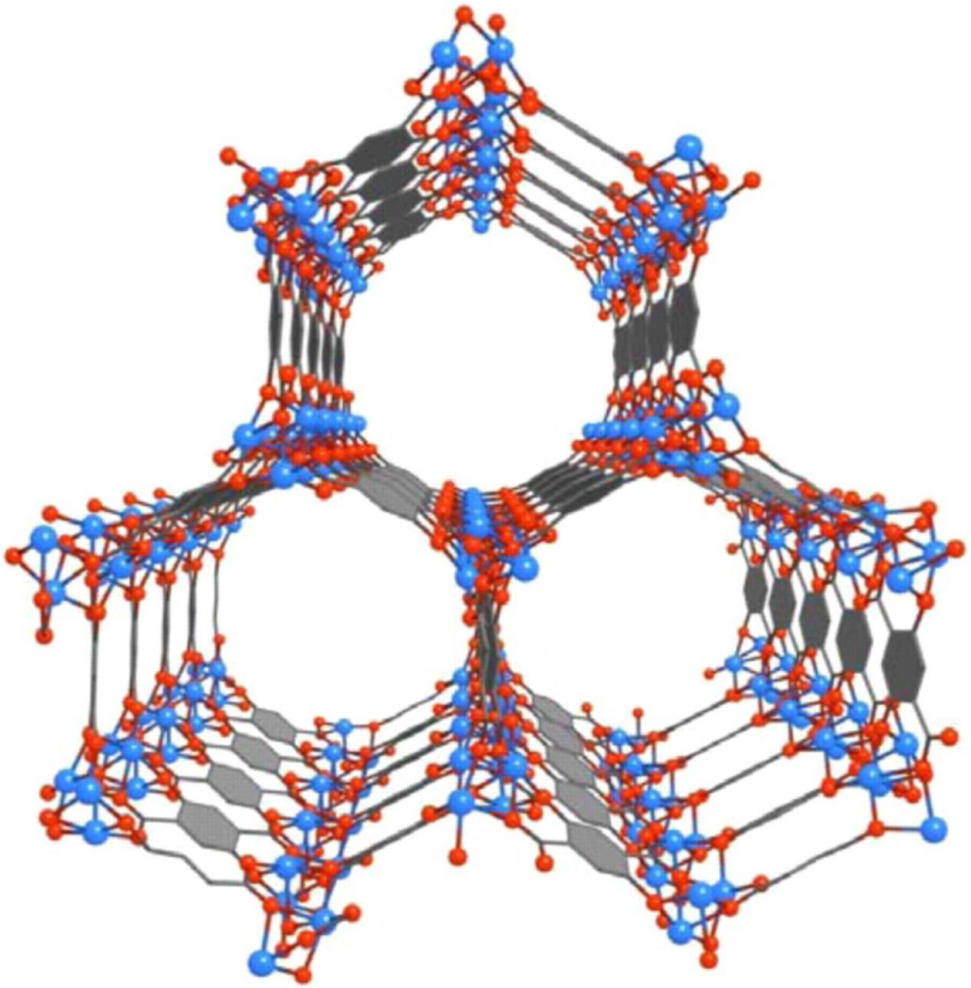


Industrial scale synthesis o solid sorbent for carbon capture

Ed Lester – The University of Nottingham

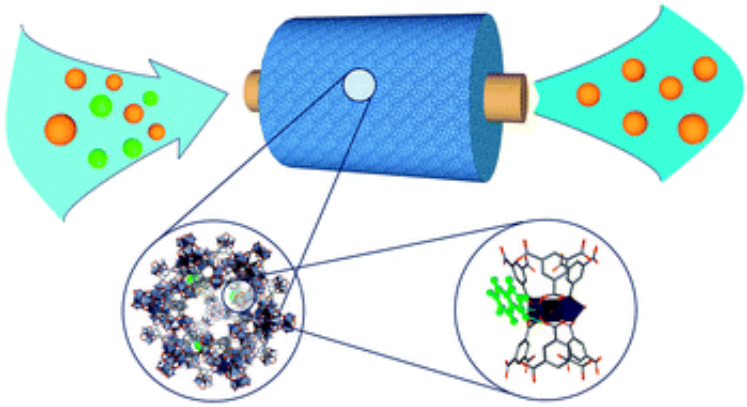
What are Metal Organic Frameworks?



- Metal ion bound to organic linkers to form a controlled geometrical structure
- Extremely high Surface Areas
- Controlled porosity
- Can preferentially adsorb certain gases
- Potential end use as $2^{nd}/3^{rd}$ gen CCS sorbents

Chem. Soc. Rev. 2014, **43**, 6173

Liquid phase separations

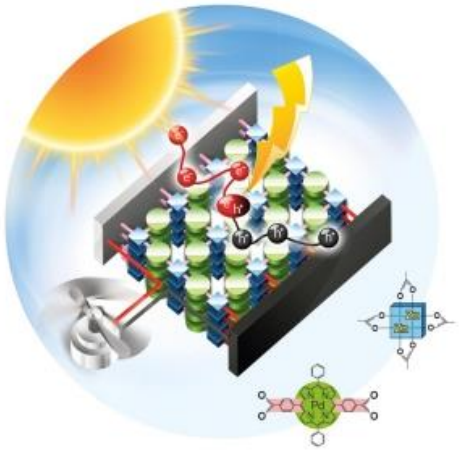


Chem. Soc. Rev. 2014, **43**, 5766

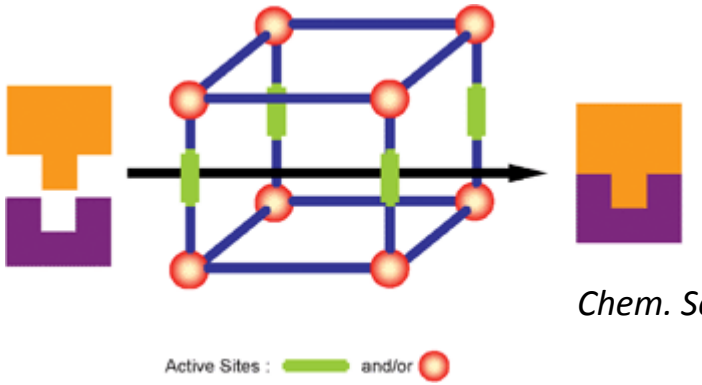
Natural Gas Storage system

MOFs

Photovoltaics



Angew. Chemie Int. Ed. 2015, **54**, 7201



Catalysis

Chem. Soc. Rev. 2009, **38**, 1450

NOW IN STORES A worker packages MOF materials produced in kilogram batches at BASF's pilot plant, in Ludwigshafen, Germany.

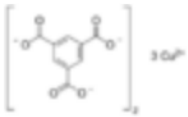
HEADING TO MARKET WITH MOFS

For **METAL-ORGANIC FRAMEWORKS,** lab-scale research is brisk as commercialization begins

MITCH JACOBY, C&EN CHICAGO

Basolite® C 300

1 Product Result | Match Criteria: Product Name



Synonym: **Copper benzene-1,3,5-tricarboxylate, Cu-BTC MOF, HKUST-1**

Empirical Formula (Hill Notation): $C_{18}H_6Cu_3O_{12}$ | Molecular Weight: **604.87**

688614 produced by BASF (Aldrich)

SDS Close

SKU-Pack Size				
688614-10G	FROM	7,150.00	0	★
688614-100G				
688614-500G				

BULK ORDERS?

ADD TO CART

e® Z1200

esult | Match Criteria: Product Name

Synonym: **2-Methylimidazole zinc salt, ZIF-8**

Empirical Formula (Hill Notation): $C_8H_{10}N_4Zn$ | Molecular Weight: **227.58** | CAS Number: **59061-53-9**

produced by BASF (Aldrich)

SDS

ack Size	Availability	Price (GBP)	Quar
10G	Available f		
100G	Estimated	4,470.00	0
500G	Only 5 lef		

asolite® A100

roduct Result | Match Criteria: Product Name

ionym: **Aluminum terephthalate, MIL-53(Al)**

pirical Formula (Hill Notation): $C_8H_5AlO_5$ | Molecular Weight: **208.10**

688738 produced by BASF (Aldrich) SDS Close

SKU-Pack Size	Availability			
688738-10G	Only 1 left in	1,108.00	0	
688738-100G	Available to s	4,172.00	0	
688738-500G	Only 2 left in			

BULK ORDERS?

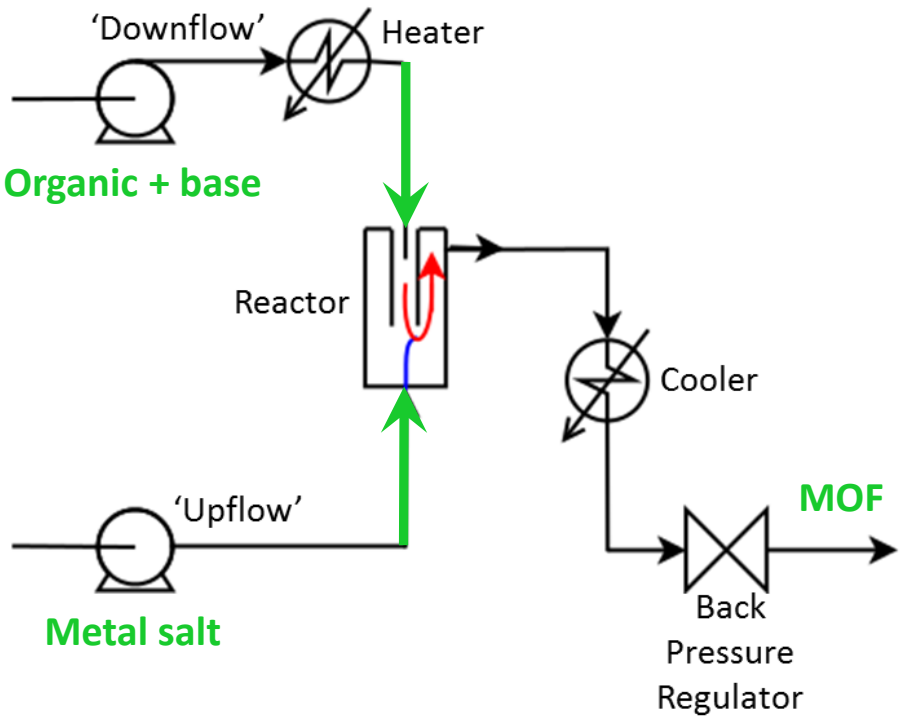
ADD TO CART

Continuous production technology…

Continuous Production of MOFs

- HKUST-1 (Cu)
- CPO-27 (Ni)
- ZIF-8 (Zn)
- ZIF-67 (Co)
- MOF-5 (Zn)
- UiO-66-COOH (Zr)

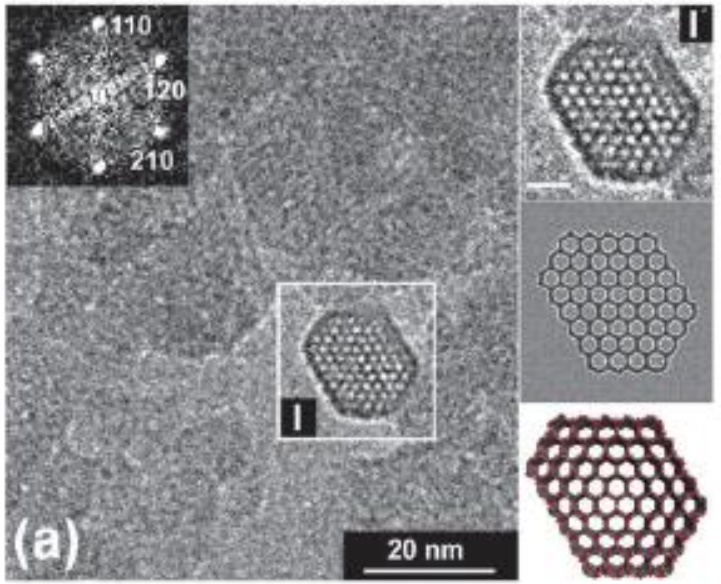
General Synthesis Method



Instant MOFs: continuous synthesis of metal organic frameworks by rapid solvent mixing†

Miquel Gimeno-Fabra,[a] Alexis S. Munn,[b] Lee A. Stevens,[a] Trevor C. Drage,[a] David M. Grant,[a] Reza J. Kashtiban,[c] Jeremy Sloan,[c] Edward Lester*[a] and Richard I. Walton*[b]

Received 22nd June 2012, Accepted 7th September 2012
DOI: 10.1039/c2cc34493a



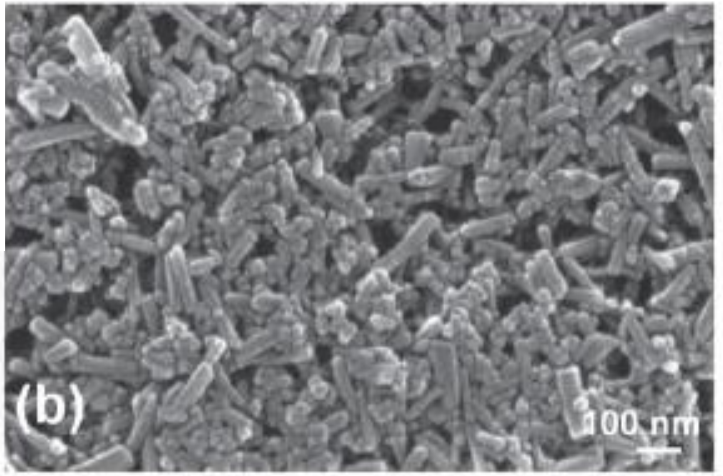
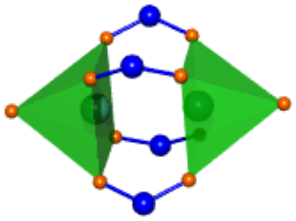


Table 1 Textural properties of HKUST-1 and Basolite C300 (Sigma-Aldrich). V_p is total pore volume at 0.95 p/p^o, and V_m micropore volume by t-plot analysis (Harkins and Jura)

Sample	BET_{SA} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	V_m ($cm^3\ g^{-1}$)
HKUST-1	1950	0.80	0.77
Basolite C300	1694	0.72	0.70

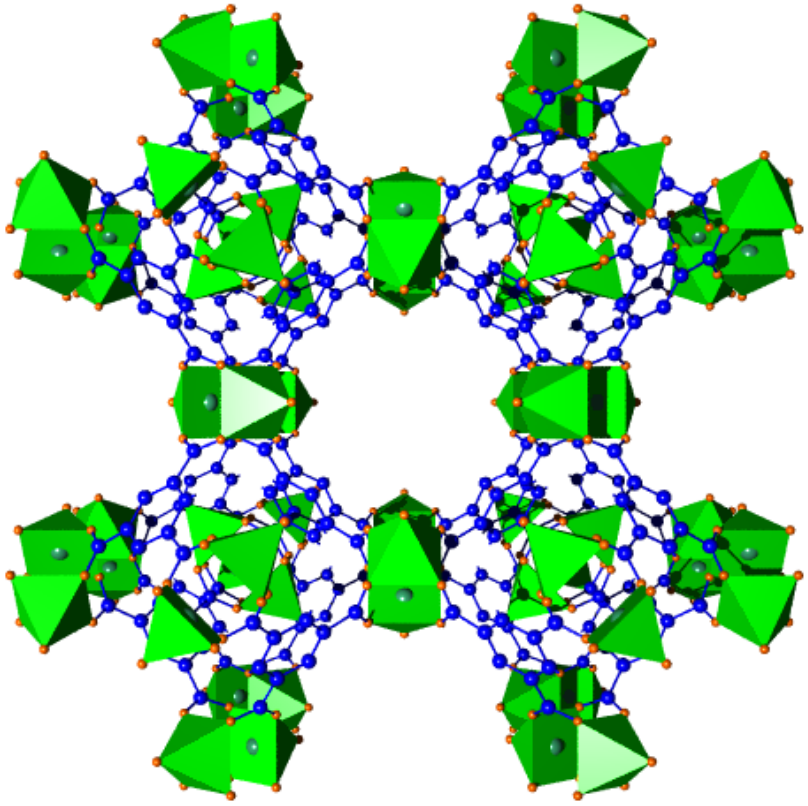
HKUST-1

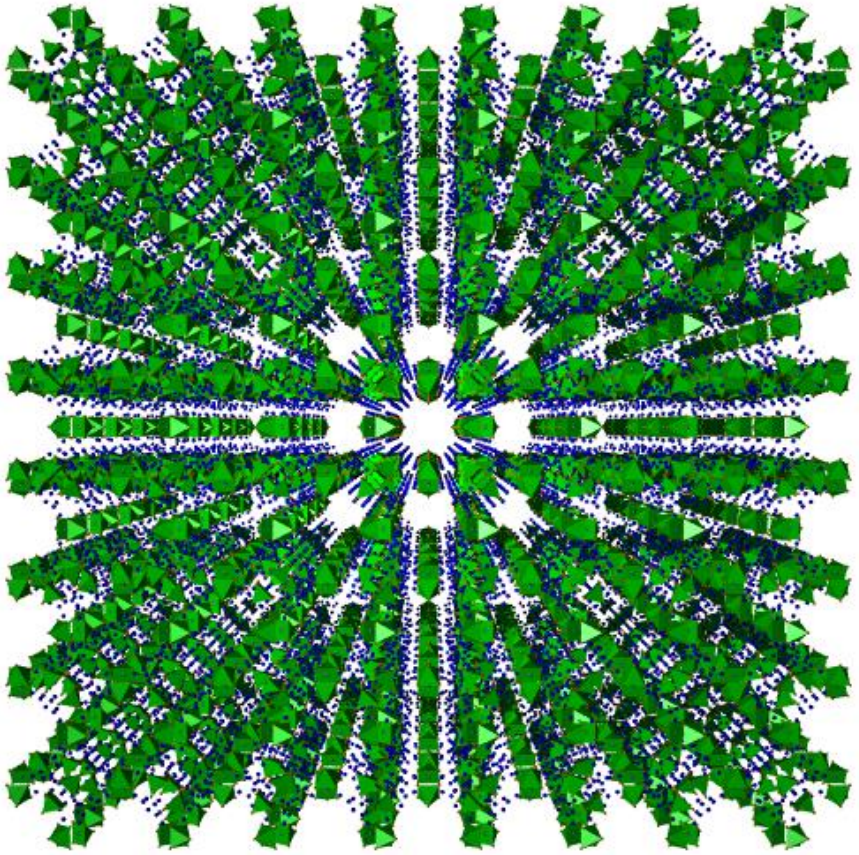
"Hong Kong University of Science and Technology"



1,3,5- tricarboxylic acid

Cu^{2+} (square pyramidal dimer)

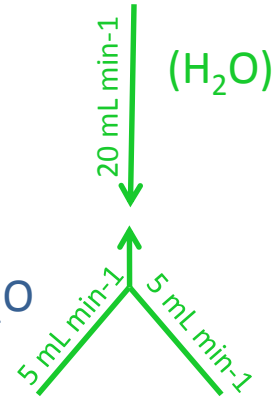




Chem. Commun., 2012,**48**, 10642-10644

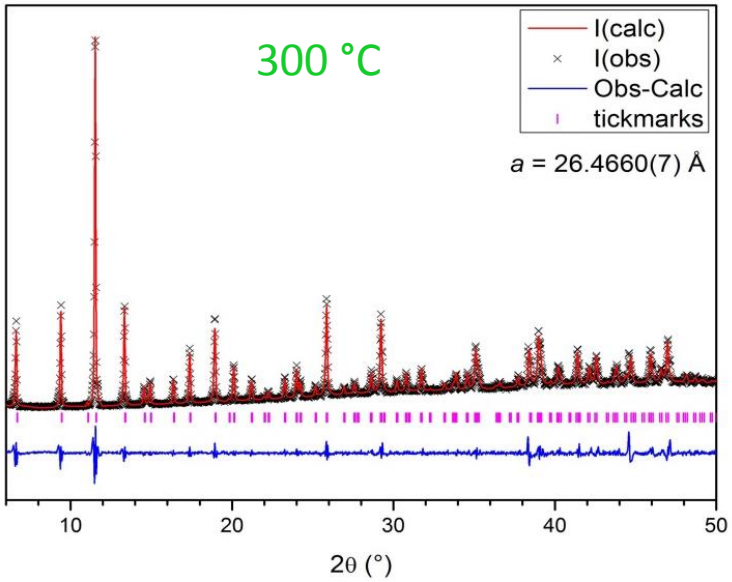
HKUST-1: $Cu_2(C_6H_3\text{-}(CO_2)_3)\cdot nH_2O$

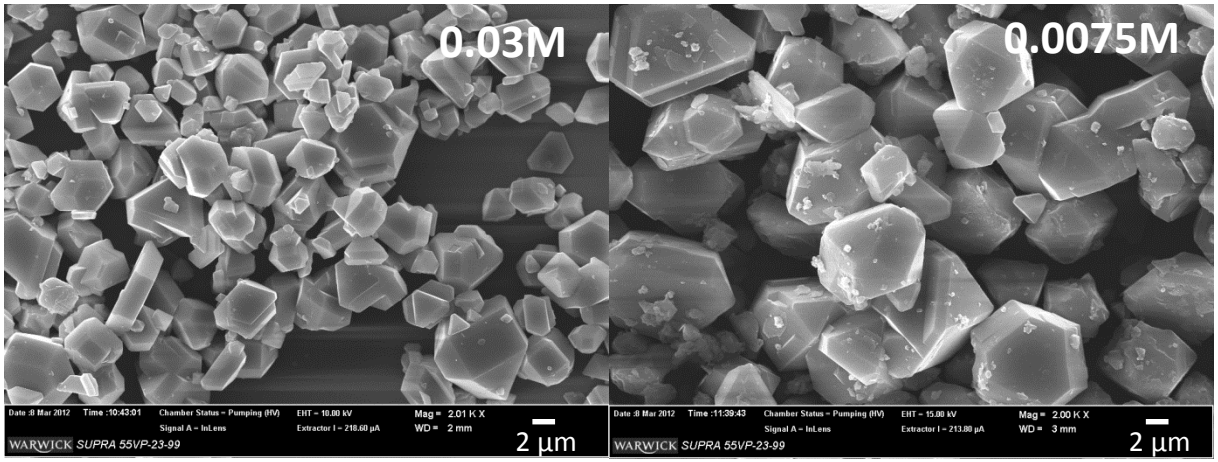
Synthesis based on standard batch reaction



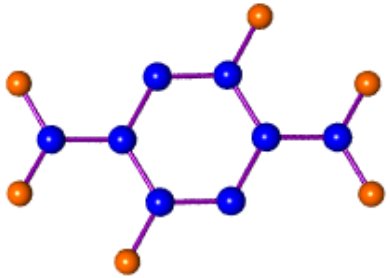
$Cu(NO_3)_2\cdot 2.5H_2O$
(DMF/EtOH)

Trimesic acid
(DMF/EtOH)



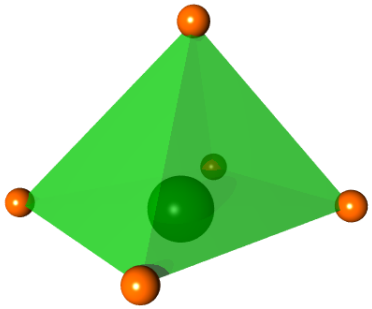


BET Surface Area = 1954 m^2/g



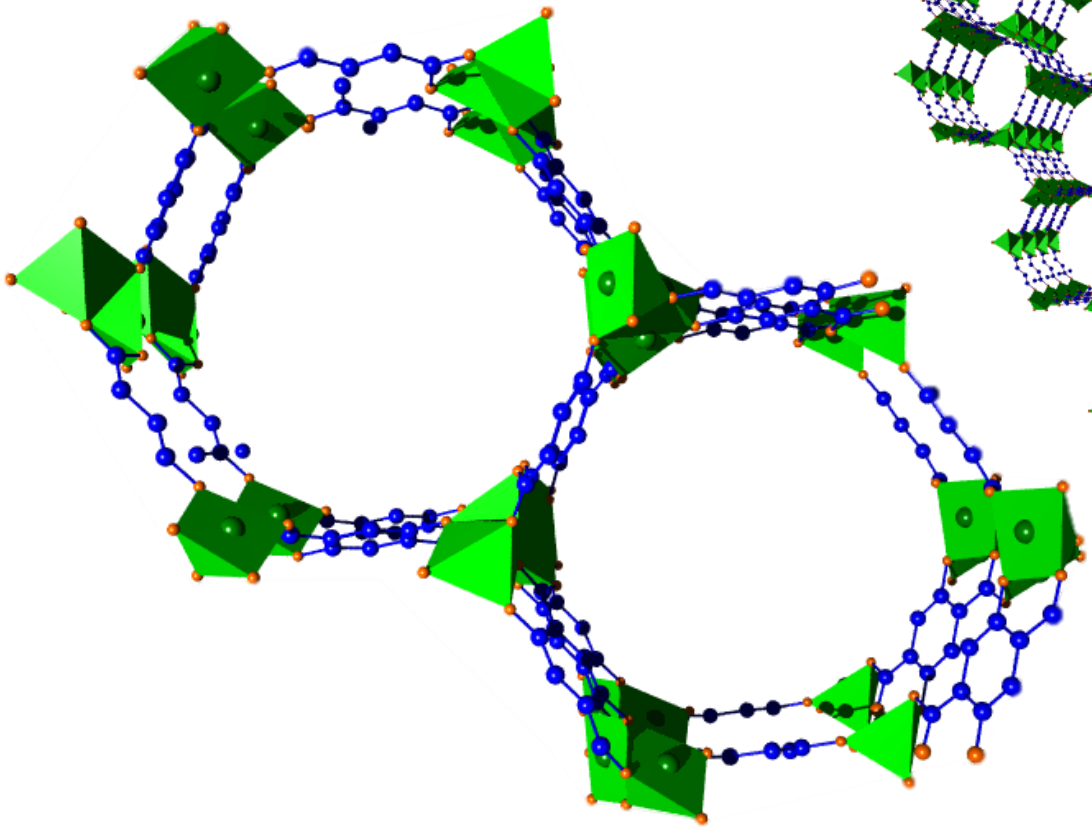
CPO-27

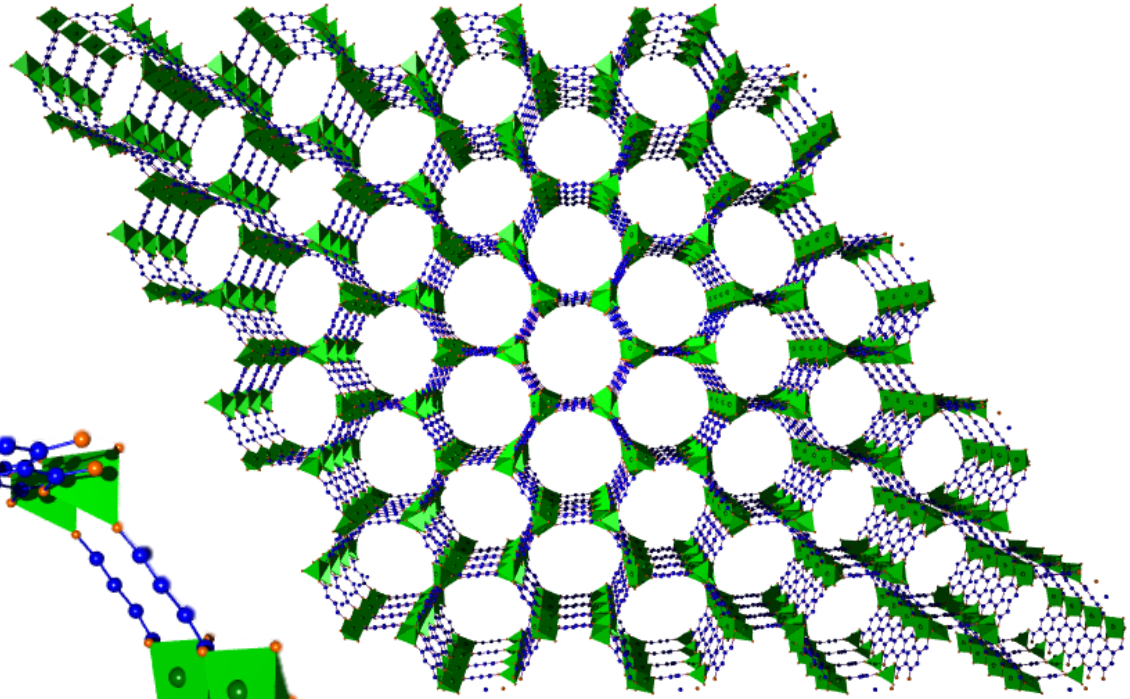
"Coordination Polymer of Oslo"



2,5-dihydroxyterephthalic acid

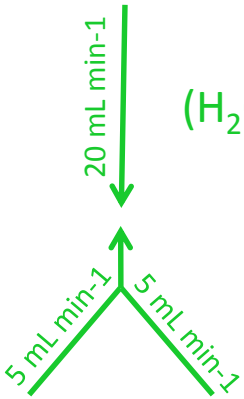
Ni^{2+} (square pyramidal)





Chem. Commun., 2012,**48**, 10642-10644

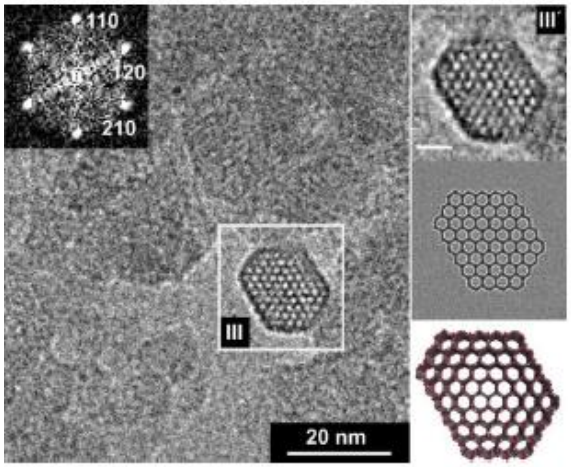
CPO-27: $Ni(CO_2\text{-}C_6H_2(OH)_2\text{-}CO_2).nH_2O$



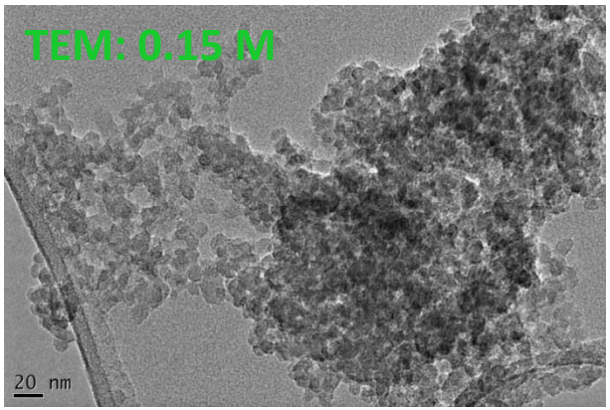
2,5-dihydroxyterephthalic acid (DMF)

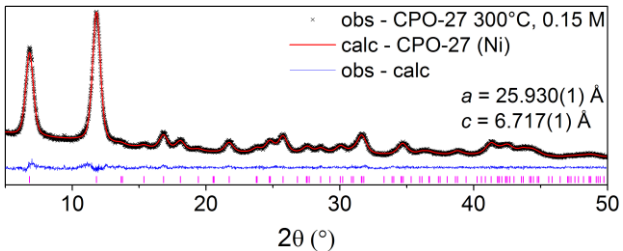
$Ni(OAc)_2 \cdot 4H_2O$ (DMF)

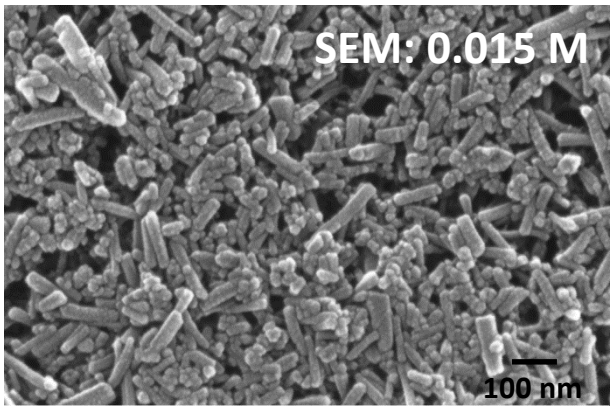
BET Surface Area = 1030 m^2/g

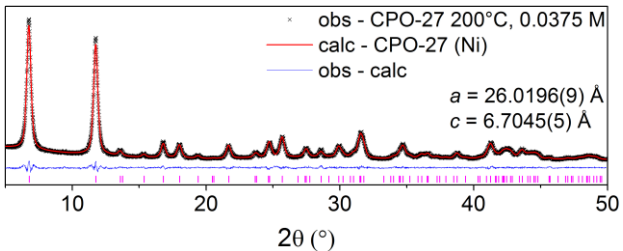


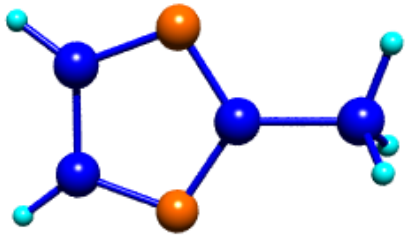
HRTEM: 0.15 M





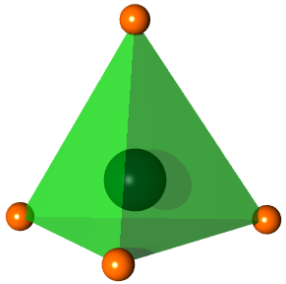






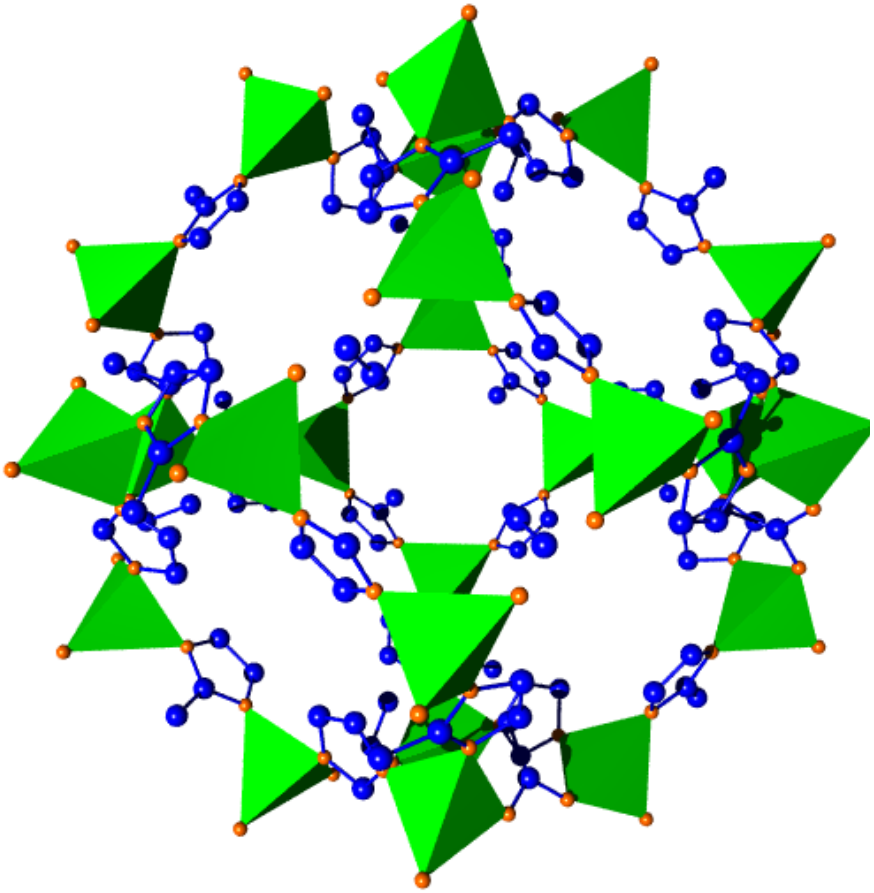
ZIF-8

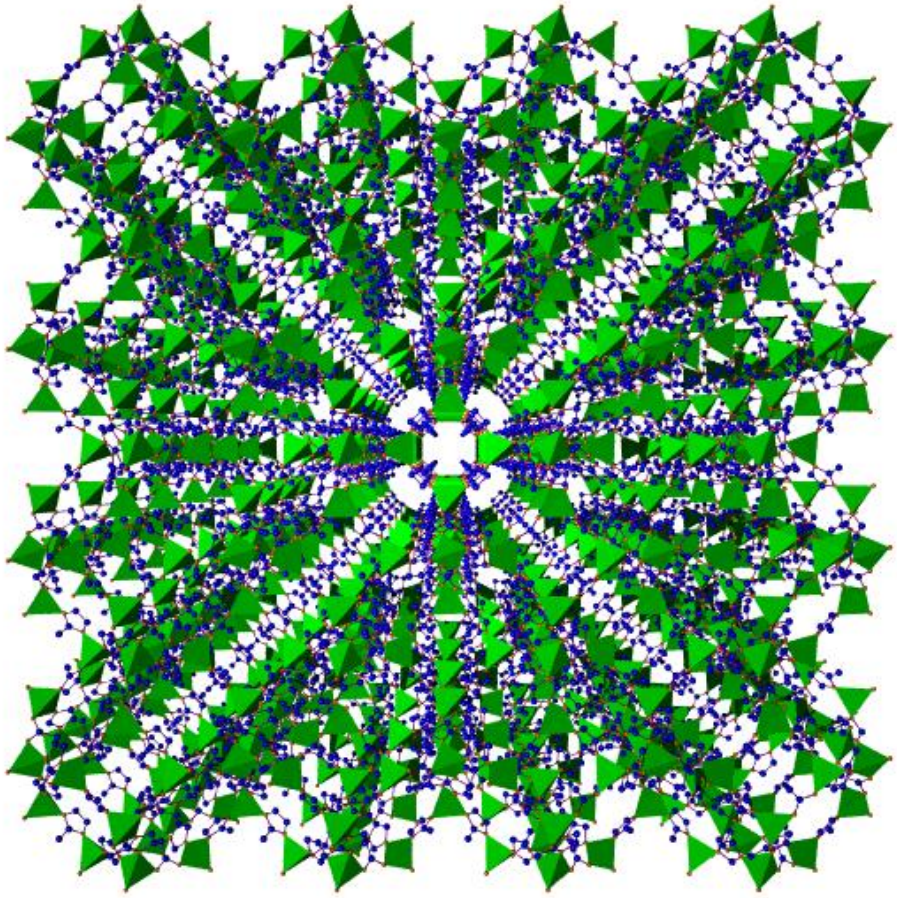
"Zeolitic Imidazolate Framework"



2-methylimidazole

Zn^{2+} (tetrahedra)

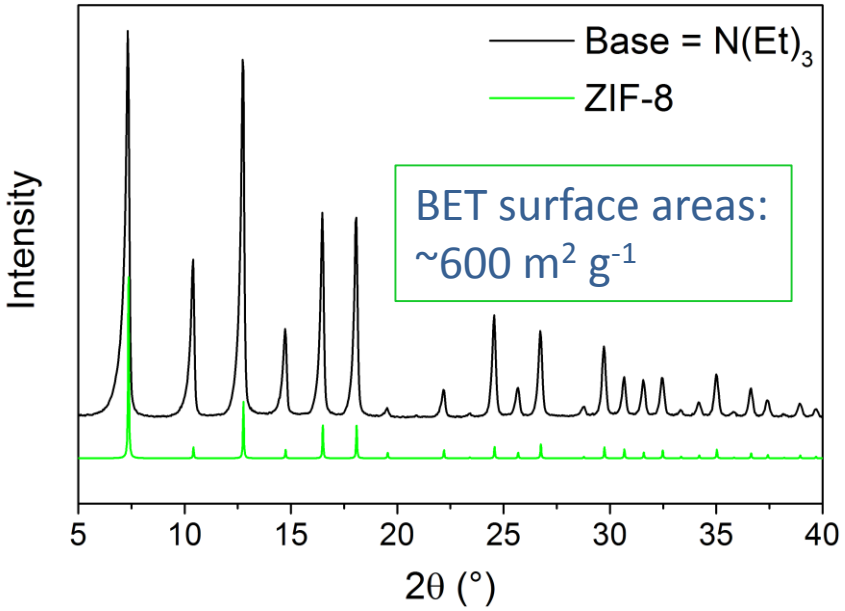




ZIF-8: $Zn(C_4N_2H_5)_2$

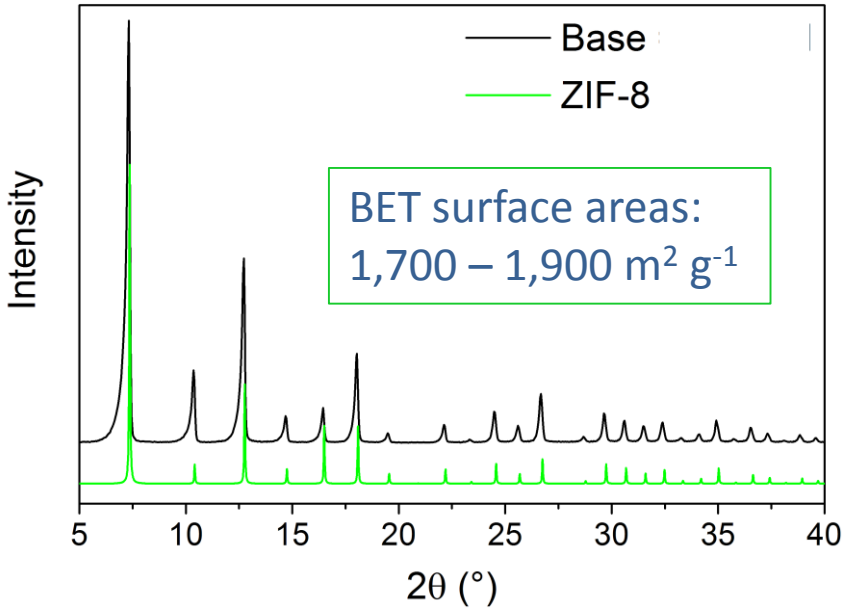
20 mL min-1 ↓ 2-methylimidazole+ **$N(Et)_3$** (water)

10 mL min-1 ↑ $Zn(OAc)_2 \cdot 2H_2O$ (water)

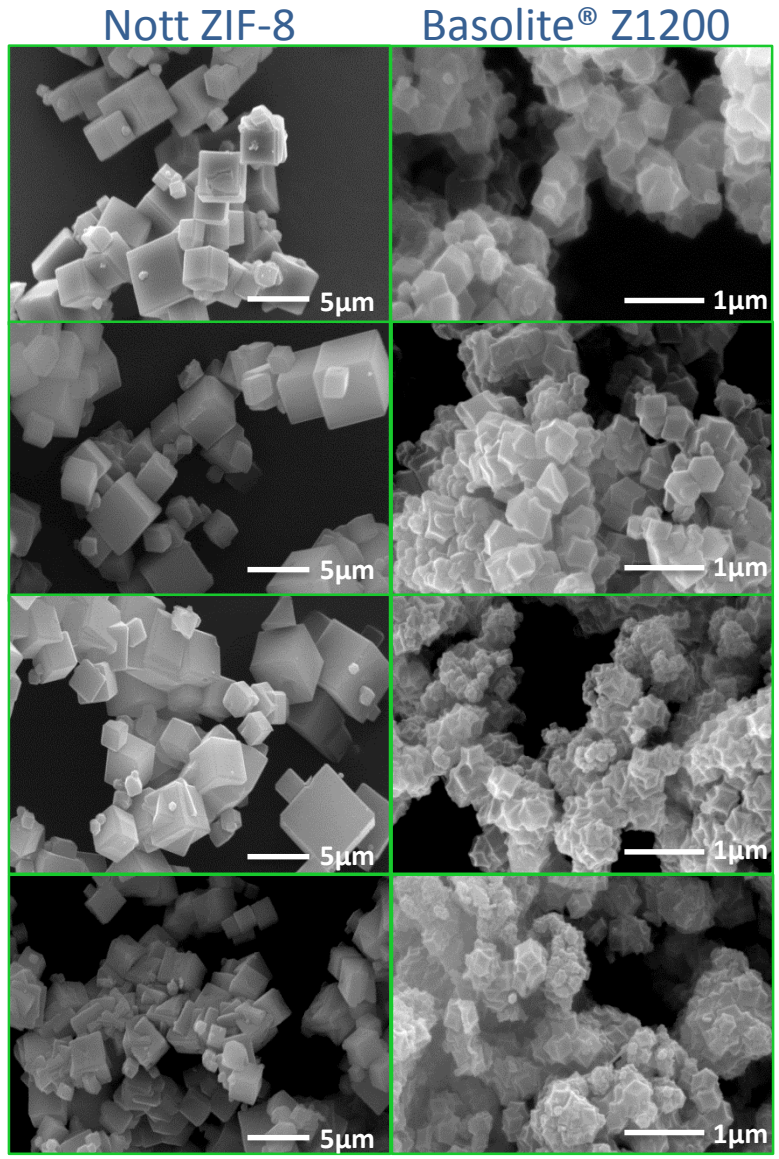


20 mL min-1 ↓ 2-methylimidazole+ Base (water)

10 mL min-1 ↑ $Zn(OAc)_2 \cdot 2H_2O$ (water)

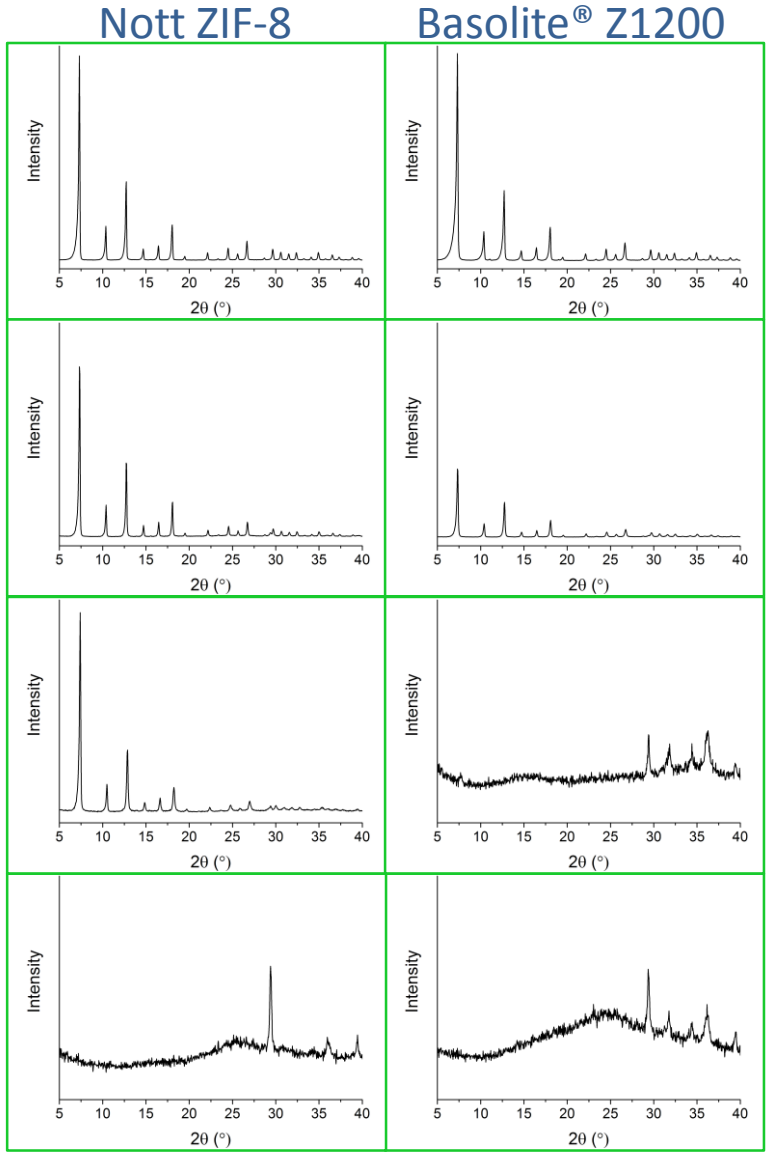


ZIF-8: Comparison (Stability)



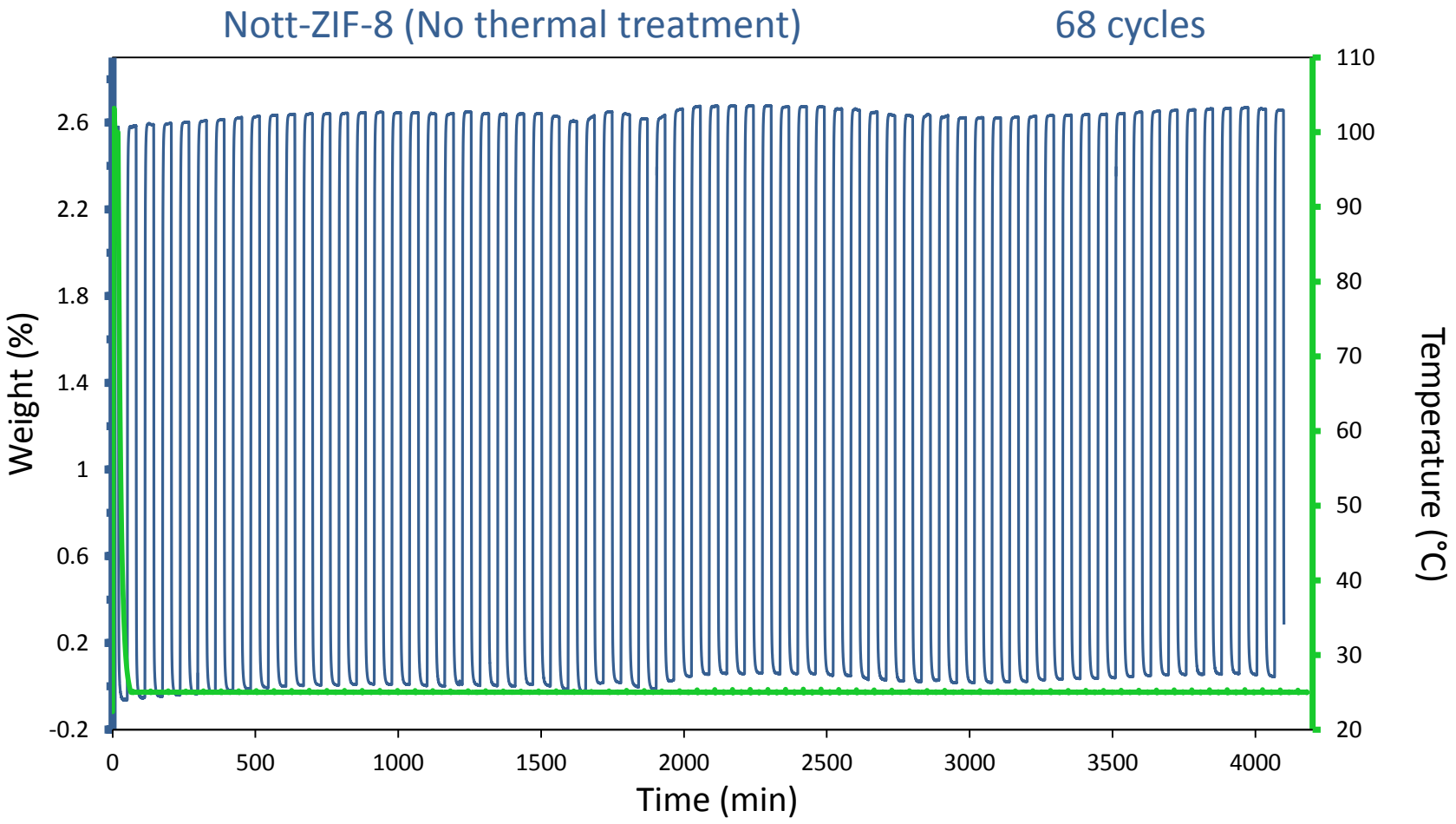
- Stability tests in nitrogen
- Average particle size:
  - Nott ZIF-8 ≈ 4 µm
  - Basolite ≈ 500 nm

ZIF-8: Comparison (Stability)



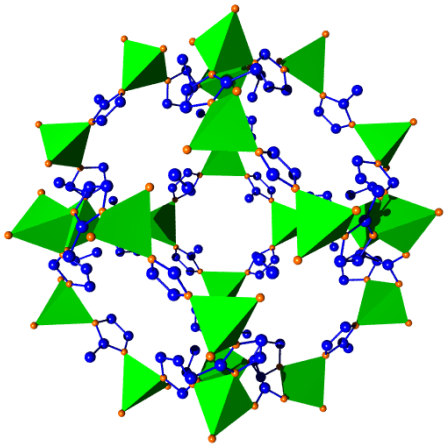
- Stability tests in nitrogen
- Average particle size:
  - Nott ZIF-8 ≈ 4 µm
  - Basolite ≈ 500 nm
- Nott ZIF-8 retains structure to higher temperatures than commercial analogue

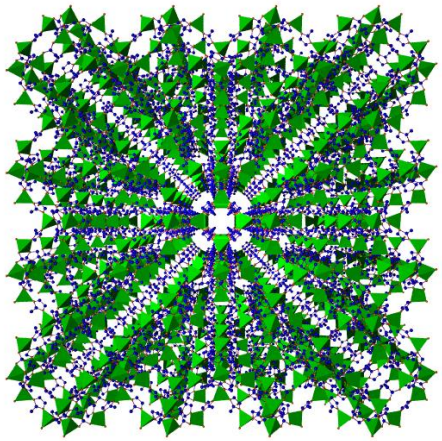
ZIF-8: CO_2 cycling



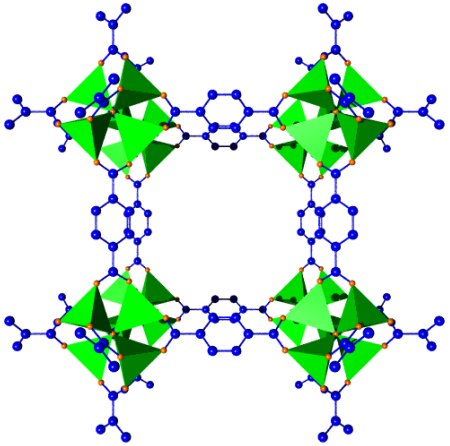
Other MOFs

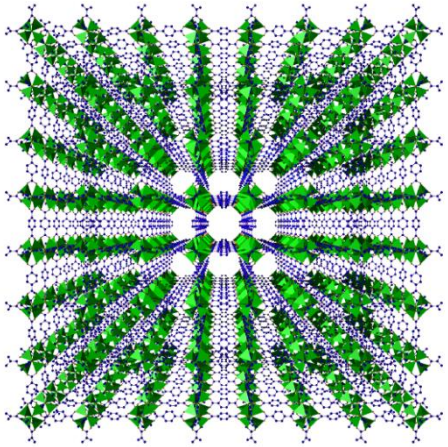
ZIF-67



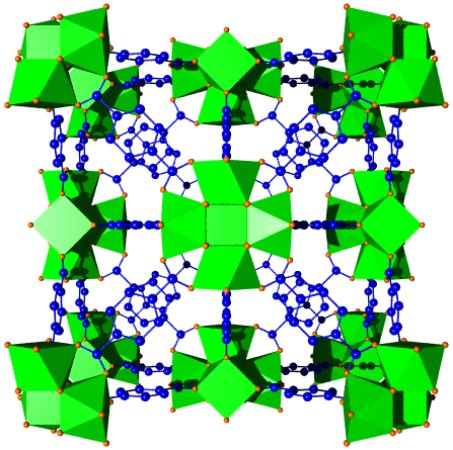


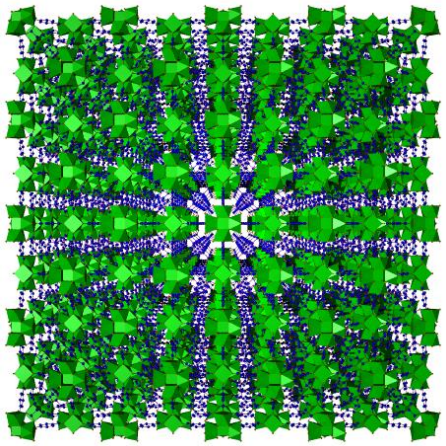
MOF-5





UiO-66-COOH





What is holding everything back?

- Very expensive MOFs
- Small scale production of MOFs
- Presentation of the MOFs – e.g. membranes/pellets etc…
- Poor understanding of the LCA of CCS with MOFs

ChemComm

COMMUNICATION

Large-scale continuous hydrothermal production and activation of ZIF-8†

Cite this: DOI: 10.1039/c5cc04636j

Received 5th June 2015,

A. S. Munn,[a] P. W. Dunne,[a] S. V. Y. Tang[b] and E. H. Lester*[a]

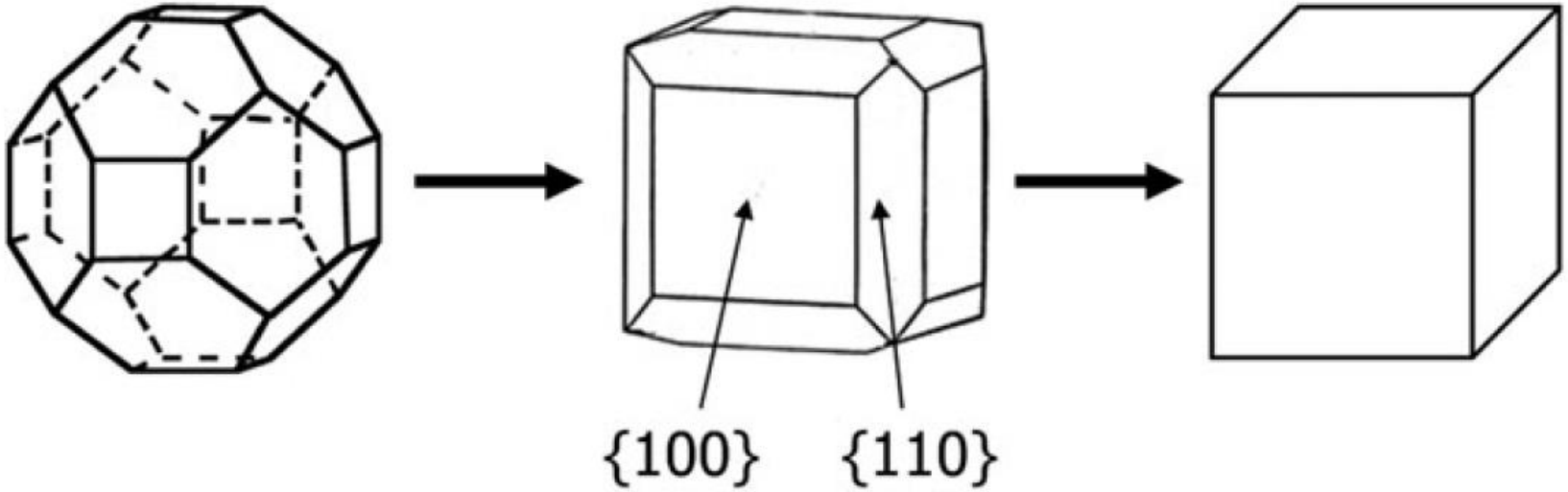
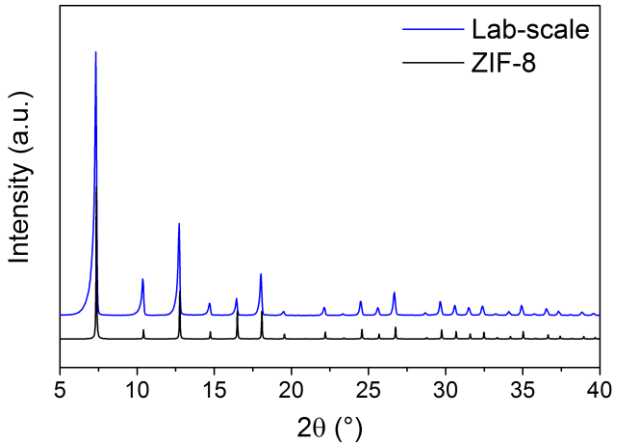
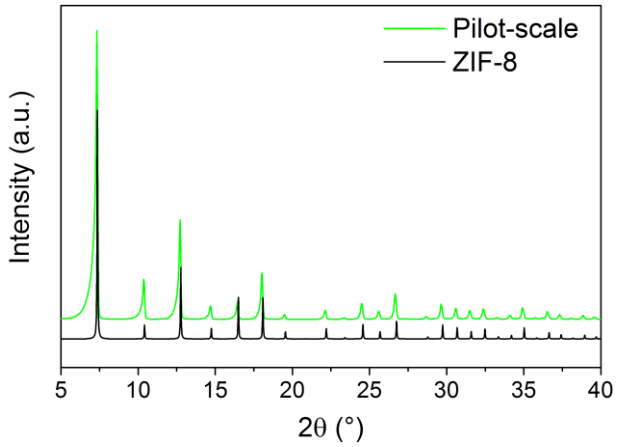


Fig. 4 Growth of truncated rhombic dodecahedron particles to form cubic particles.

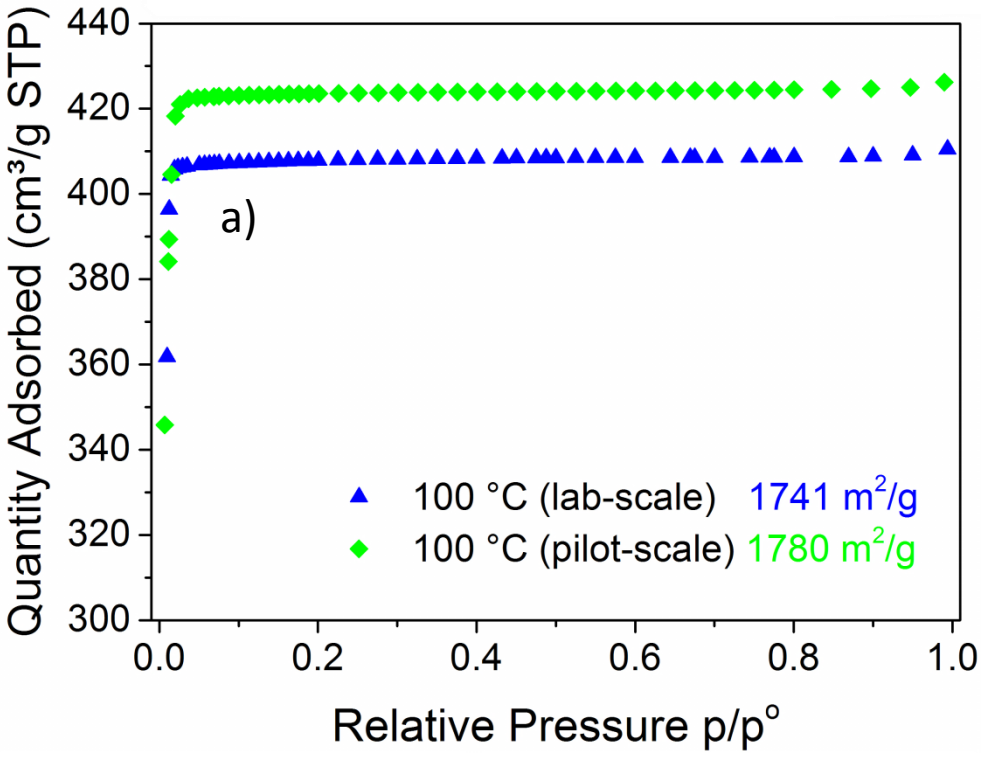
ZIF-8: Scale-up

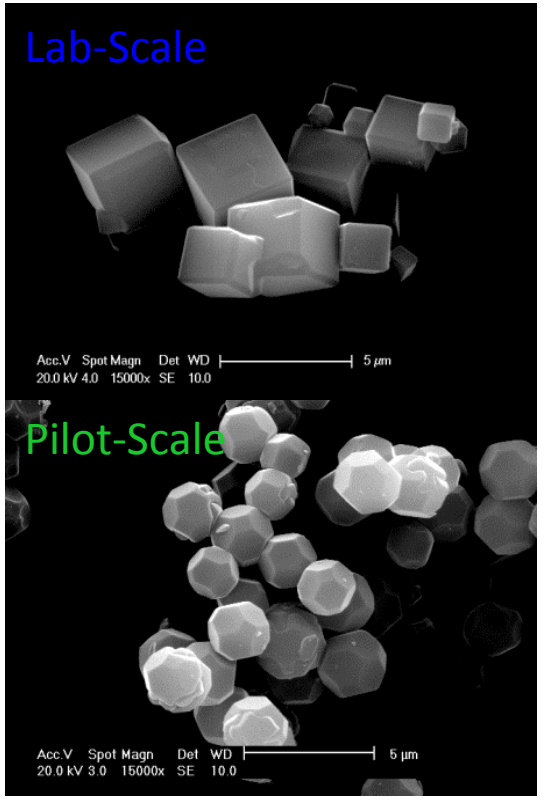
Up to 27 g h^{-1}





Up to 810 g h^{-1}





1000 ton/annum plant built as part of the FP7 funded SHYMAN project

Conclusions

SEVENTH FRAMEWORK PROGRAMME

- The real challenges for 2nd and 3rd generation sorbents are around production scales, activation and pelletisation.
- Without any meaningful demonstration of the potential for these materials, there will only be slow progress away from either no capture (with significant environmental penalties) or amine based 1st generation capture (with significant operating penalties).