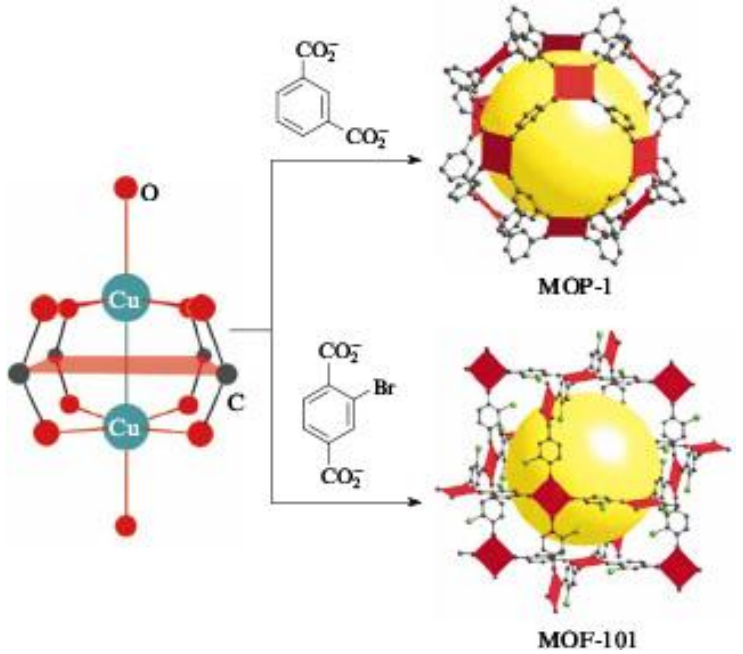
UST GLOBAL RESEARCH INTERNSHIP PROGRAM
8 WEEKS AT KIER

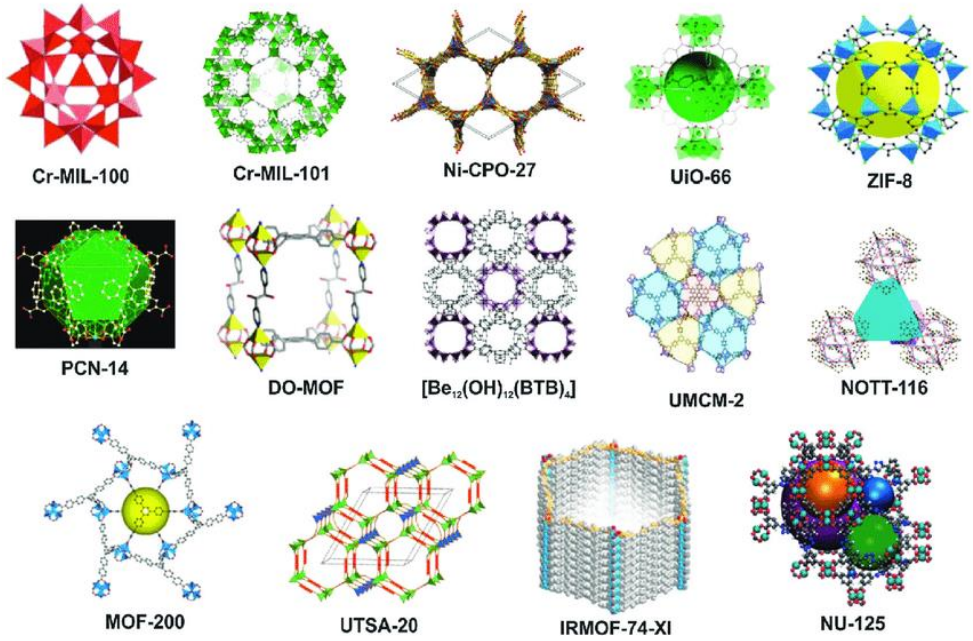
UST UNIVERSITY OF SCIENCE & TECHNOLOGY

KIER 한국에너지기술연구원 KOREA INSTITUTE OF ENERGY RESEARCH

Subject of Research: MOFs & MOPs

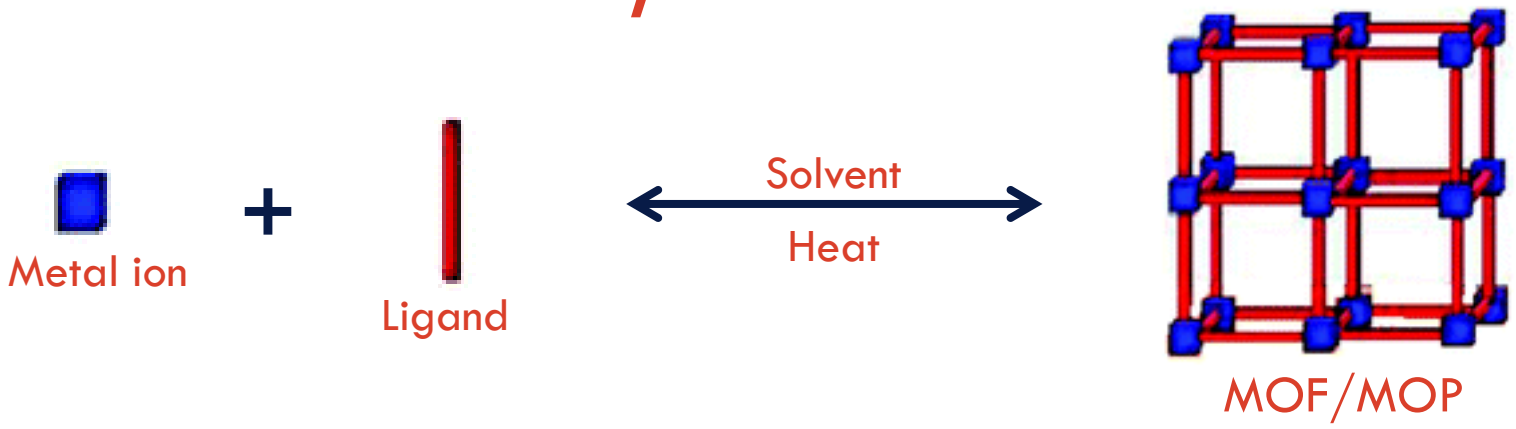
Metal-organic frameworks (MOFs) and metal-organic polyhedral (MOPs) are classes of porous materials consisting of metal ions linked together by organic ligands.





They are incredibly versatile; 20,000 structures known. With vast surface areas (~6,000 m^2/g) and tunable pore sizes, MOFs and MOPs have a range of applications including in catalysis, drug delivery and gas storage.

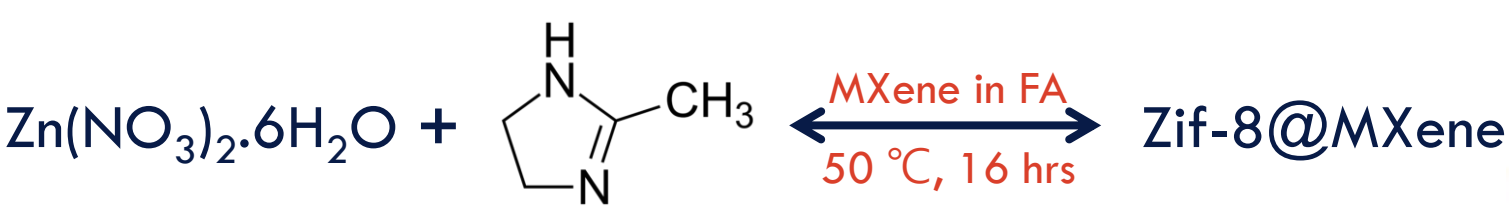
Subject of Research: Synthesis



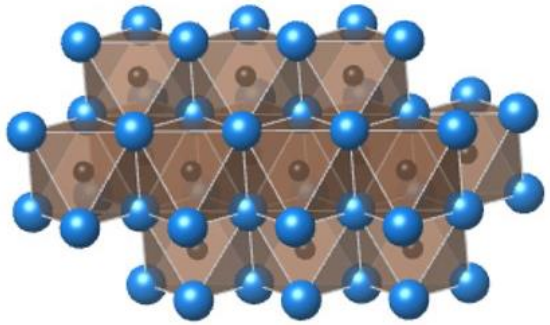
- Synthesis of MOFs and MOPs is mostly by self-assembly.
  - Equilibrium so product is most thermodynamically stable structure.
  - Structure depends on nature of ion and ligand.
- Challenges include selecting right solvent(s) and reaction conditions.
  - Exothermic reaction favours low temperatures but results in long reaction times.
  - Solvent must dissolve all reactants but still allow assembly to occur.

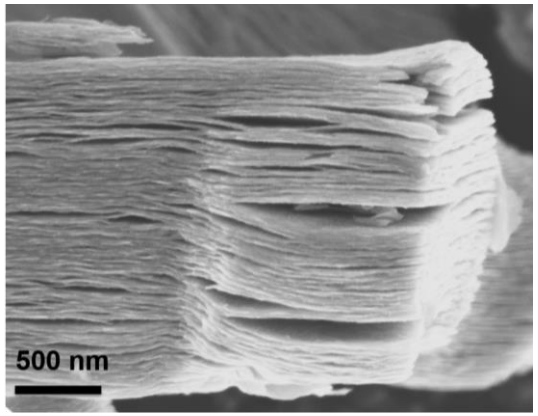
Content of Research: Weeks 1-2, Zif-8@MXene

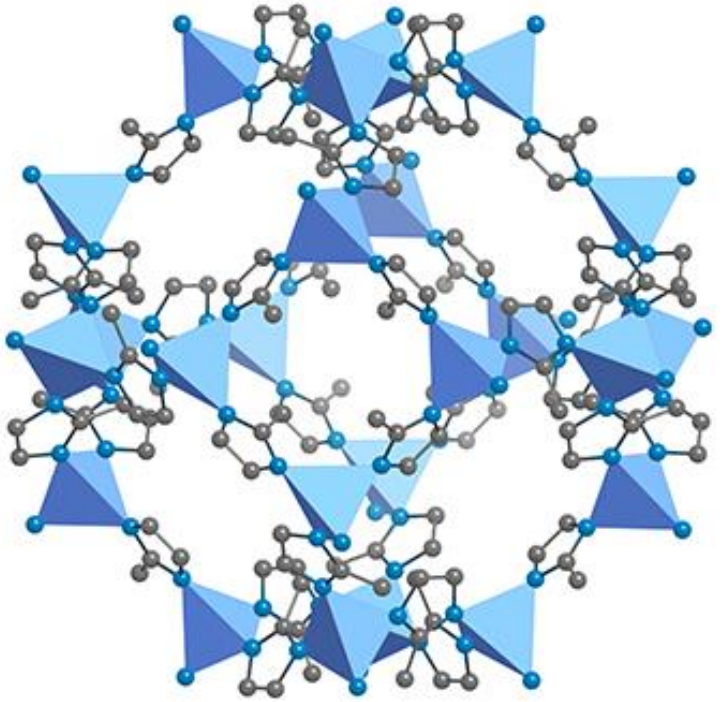
Composite material of MOF ZIF-8 and inorganic material MXene. Zif-8 can be grown between the MXene sheets:



Glass vial reaction in an oven and washing of product with methanol gave black powder.

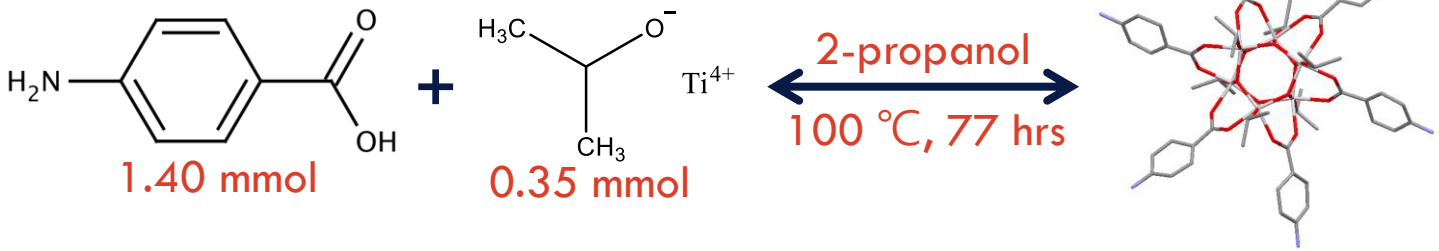


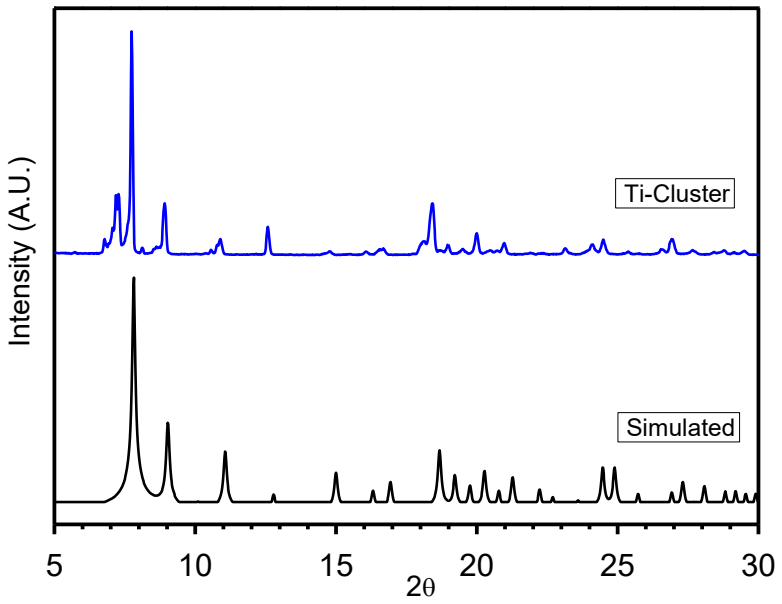




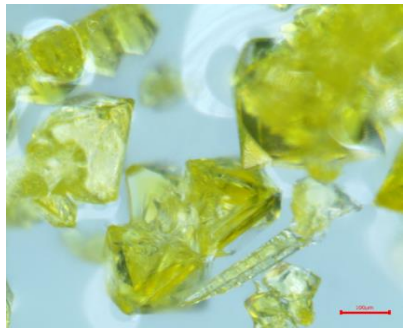
Content of Research: Weeks 1-2, TiO Cluster

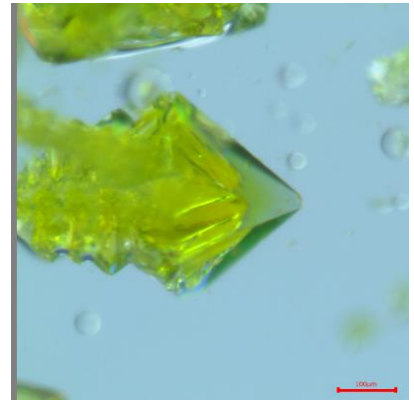
Precursor to lithium titanium oxide (LTO) structures.





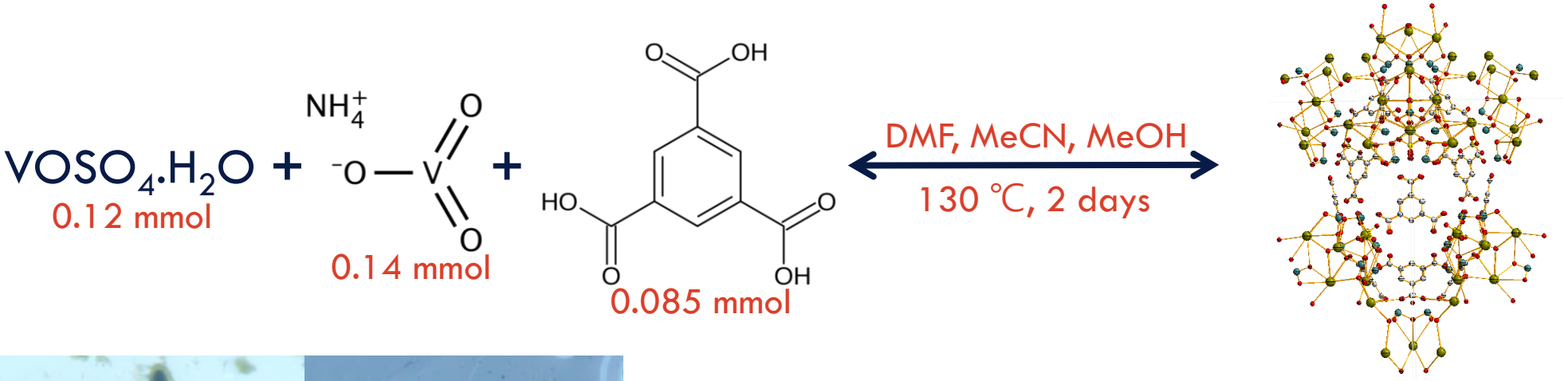
Sealed cell tube reaction gave yellow crystals after washing with 2-propanol. XRD almost matched the predicted pattern.

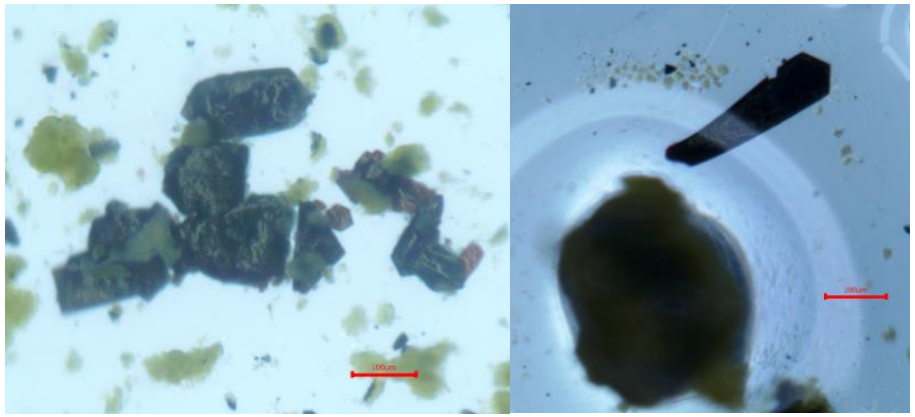




Contents of Research: Week 3 –, VMOP-24

VMOP-24 is a vanadium-based MOP structure discovered recently (N. Xu, 2019).





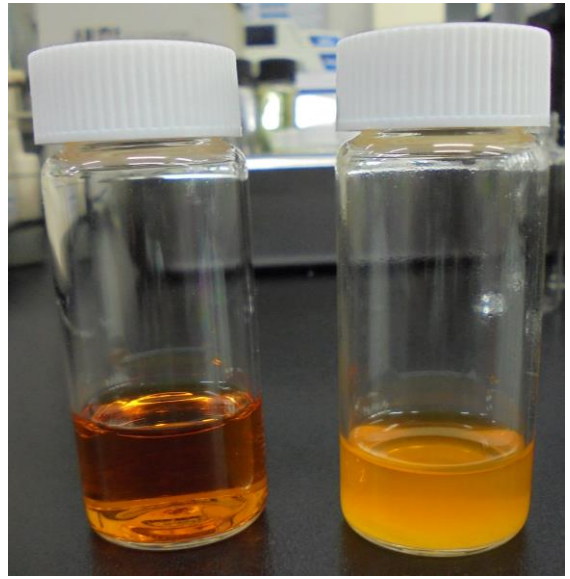
Vial and cell tube reactions gave no product. Bomb reaction gave dark green crystals but with a lot of solid impurity, even after washing with methanol.

Contents of Research: Week 3 –, VMOP-24

Potential issues identified included NH_4VO_3 not dissolving in solvent mix (2 mL DMF, 0.25 mL MeOH, 0.25 mL MeCN). Solubility tests were carried out to find suitable solvent mixtures. Addition of H_3BTC increased solubility.

Solvent Mixture (mL)	Solubility of NH_4VO_3
DMF, MeOH, MeCN 2:0.25:0.25	Not soluble
DMF, MeOH, MeCN 2:1:1	Partially soluble
DMF, MeOH, MeCN 2:2:2	Soluble after H_3BTC
Reported mixture + H_2O (2)	Soluble
Reported mixture + H_2O (1)	Soluble

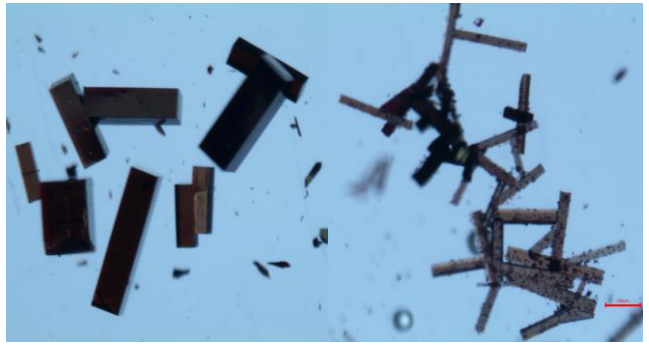
NH_4VO_3 in H_2O 1 mL (left) and 2 mL (right)



DMF, MeOH, MeCN 2:2:2

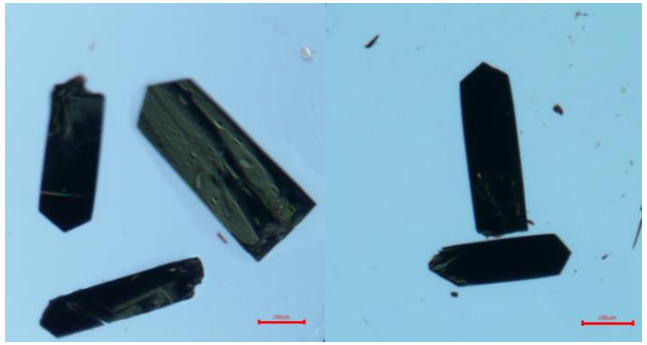
DMF, MeOH, MeCN 2:1:1

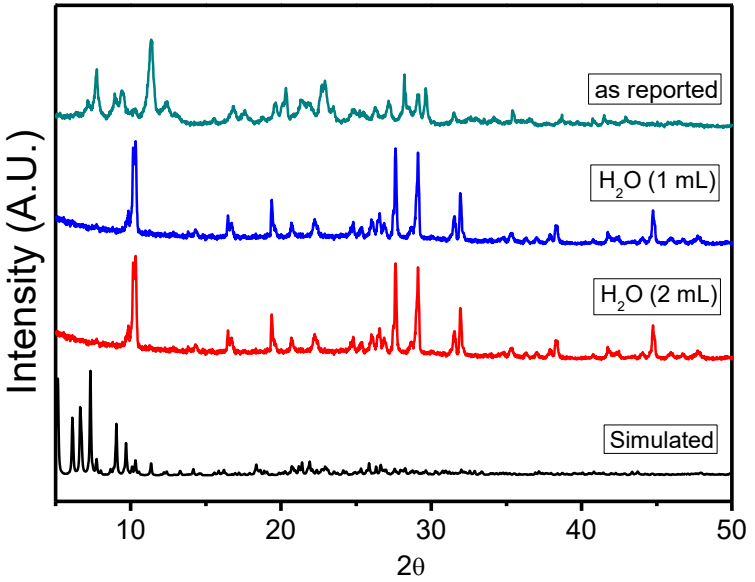
Contents of Research: Week 3 –, VMOP-24



Reaction when 1 mL water was added to original solvent mixture. Less impurity observed.

Reaction when 2 mL water was added to original solvent mixture. Largest crystals.



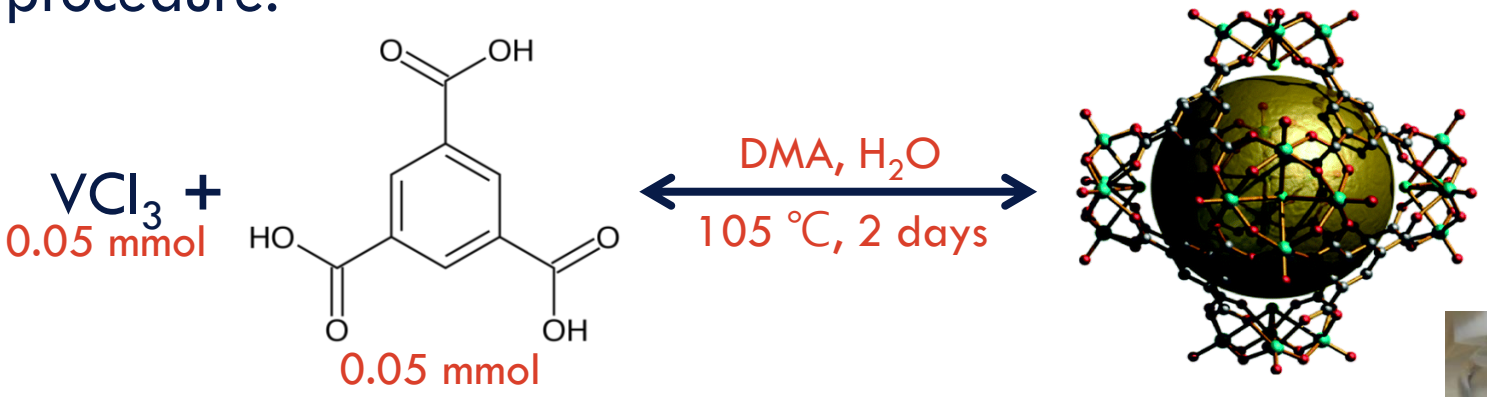


XRD shows better crystallinity after water addition but it does not fully match the predicted pattern.

Reaction in 2 mL DMF, MeOH and MeCN is in progress (16/08/19)

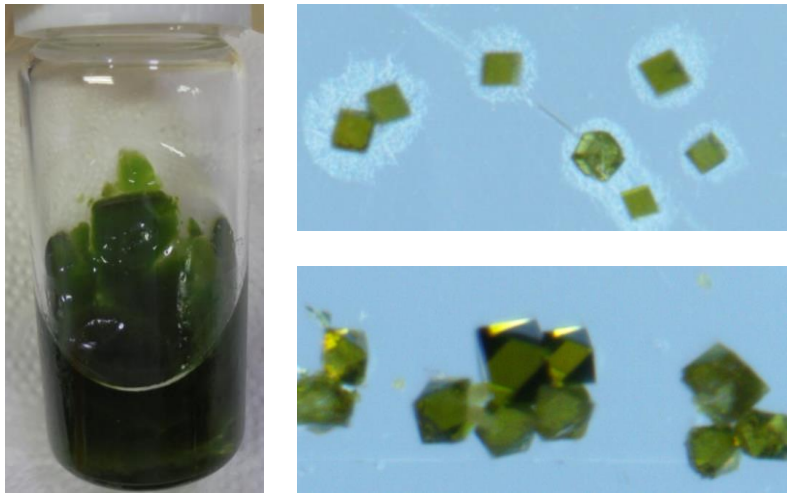
Contents of Research: Week 3 –, Hyball-3

Another known vanadium-based MOP (Z. Zhang, 2014) with an easier synthetic procedure.



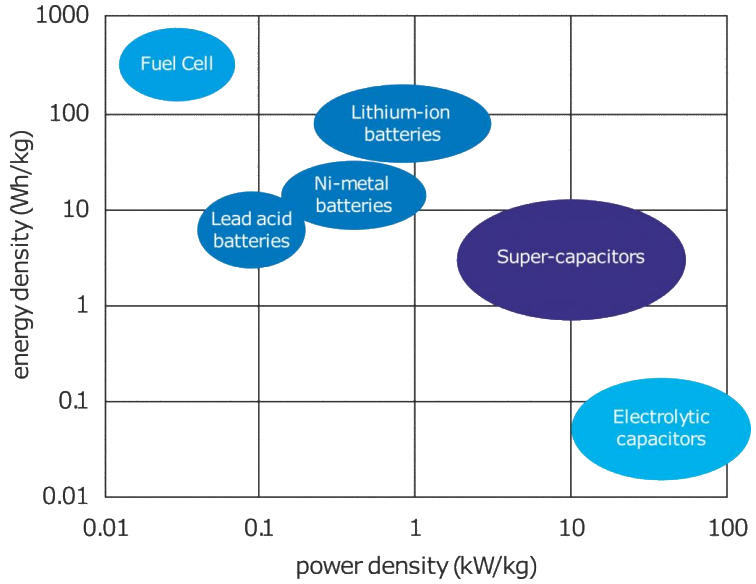
VCl_3 added to H_3BTC using a glove box as it is air sensitive.

Reported synthesis gives dark green crystals. 5x scale-up vial reaction gives a green jelly. Better crystals obtained by washing jelly with methanol. 10x scale-up gave no product.

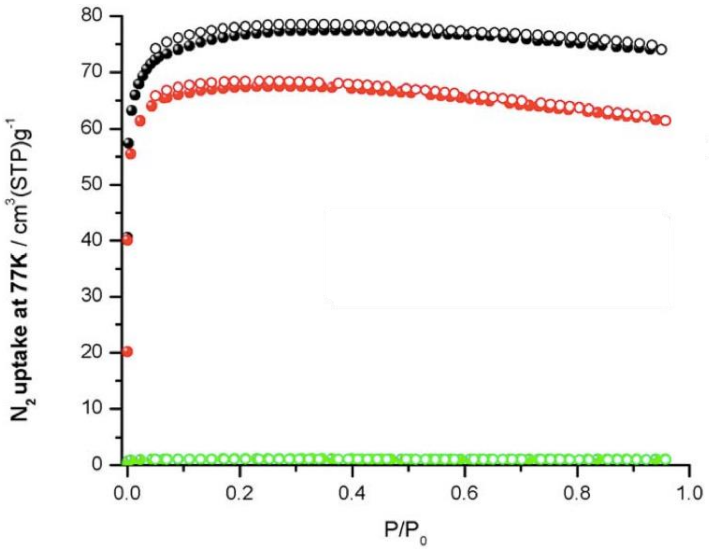


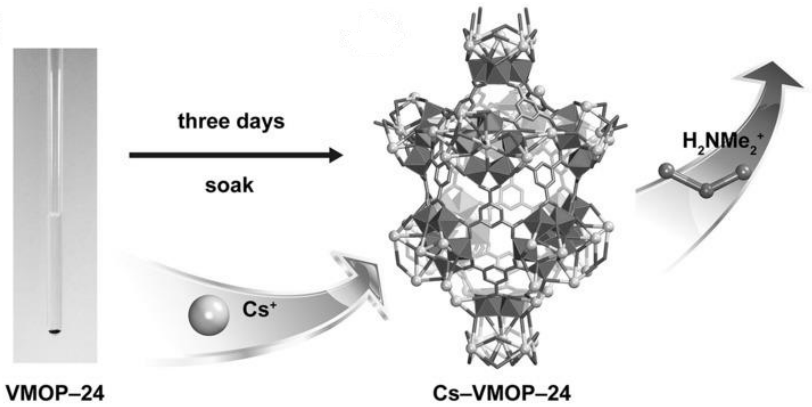
Further Investigations

All compounds synthesized are being researched as potential supercapacitor materials. Supercapacitors have high power densities but low energy densities compared to batteries.



BET isotherms measure surface area.





Cation exchange (ICP, NMR) gives indication of energy density.
Composites with carbon structures (eg. CNTs).