Synthesis of Functionalized Metal-organic Frameworks

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Abstract

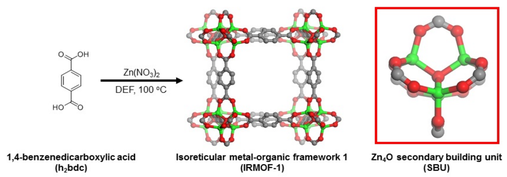


Figure 1. IRMOF-1 shows the basic crystal structure of a MOF.

Metal-organic frameworks (MOFs) are comprised of metal clusters and organic ligands. MOFs, similar to zeolite, carbon nanotubes, and activated carbon, have very porous structures. Since MOFs have many more building blocks than materials such as zeolite, The properties of MOFs can be changed via the functionalization of the ligand. The functionalization of the MOF could be achieved by modifying ligands before the synthesis of the MOF (pre-synthetically) or after the synthesis of the MOF (post-synthetically). These functionalized MOFs can be used for numerous applications such as gas storage, gas separation, and catalysis.

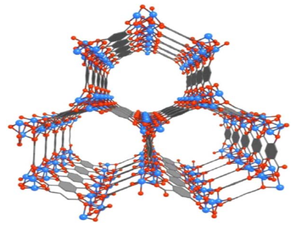


Figure 2 Similar to a honey comb, the structure of MOFs allows them to be extremely porous and have extremely high surface area.

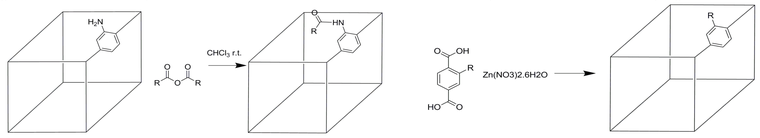


Figure 6 This depicts a basic post synthetic modification of the functionalized group.
Figure 7 This depicts a basic pre synthetic modification of the functionalized group.

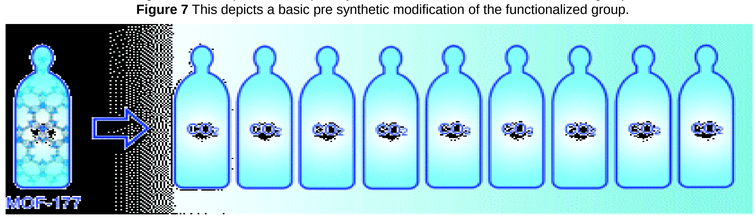


Figure 3 MOFs are able to store large quantities of gases without extremely high pressure

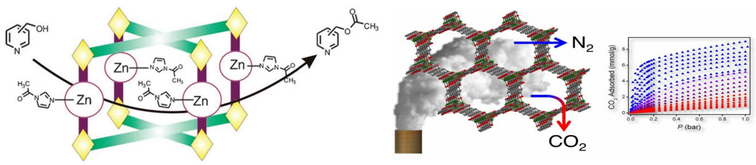
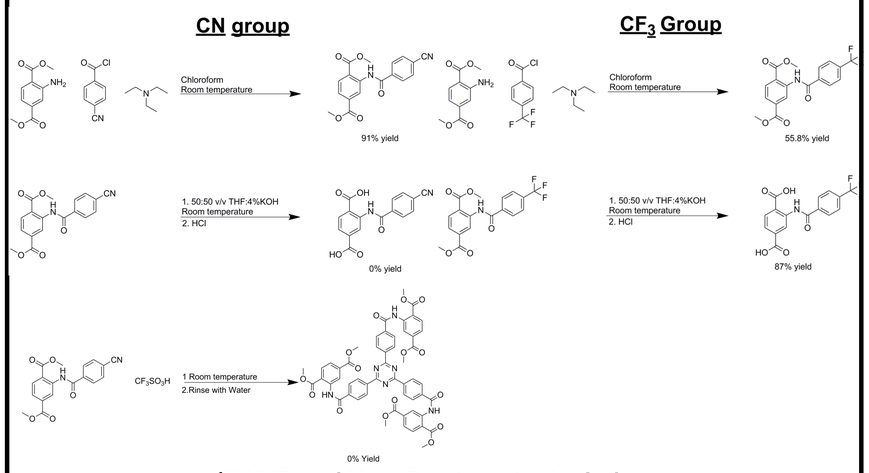


Figure 4 The MOF can act as a catalyst by combining its functionalized group with a material.
Figure 5 MOFs can be used as filters to separate carbon dioxide out of smoke to prevent it from getting into the air.

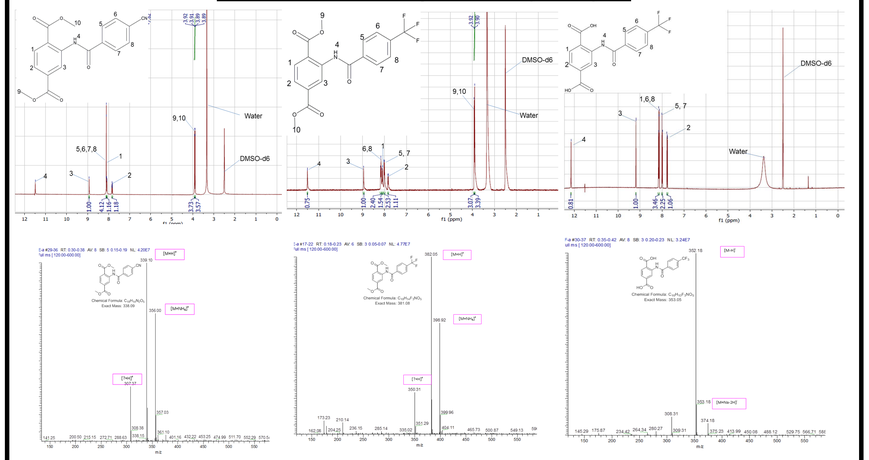
In this project, our goals are to synthesize two ligands functionalized with CF_3 and the other with CN. Only the CF_3 functionalized ligand is synthesized to form a MOF. The MOF that forms will help to see how the functionalized group affects the structure of the MOF.

http://theconversation.com/mof-the-chart-why-a-record-breaking-surface-area-matters-9915
http://www.greencarcongress.com/2005/12/metalorganic_fr.html
http://newscenter.lbl.gov/2013/11/22/an-inside-look-at-a-mof-in-action/
http://alchemy.cchem.berkeley.edu/metal-organic-frameworks.html

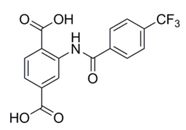
Synthesis of Ligands



^{1}H NMR and Mass Spectrometry Analysis

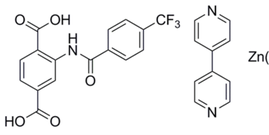


Synthesis of MOFs



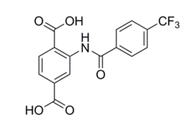
Zn(NO3)2.6H2O

Experiment	Conditions	Observations
1	DMF 120 °C for 24 Hours	No crystals formed
2	DMF 35-100°C in 30 minutes, 100°C 24 hours 100-35 °C in 30 minutes	No crystals formed
3	DMF 85°C for 48 hours, 135°C 48 hours	No crystals formed
4	DMF 120°C for 72 hours with different ratios	1:1 no crystals; light yellow solvent 1:2 no crystals; less yellow solvent 1:3no crystals; less yellow solvent 1:4 no crystals clear 1:5 no crystals clear
5	DEF 120°C for 48 hours	Red small crystals formed on sides appear to be cubes of some form



Zn(NO3)2.6H2O

Experiment	Conditions	Observations
1	DMF 120 °C for 24 Hours	No crystals formed
2	DMF 35-100°C in 30 minutes, 100°C 24 hours 100-35 °C in 30 minutes	Small yellow crystals formed
3	DMF 120°C for 72 hours	Solvent turned slightly yellow
4	DEF 120°C for 48 hours	Red medium crystals formed on sides appear to be cubes of some form

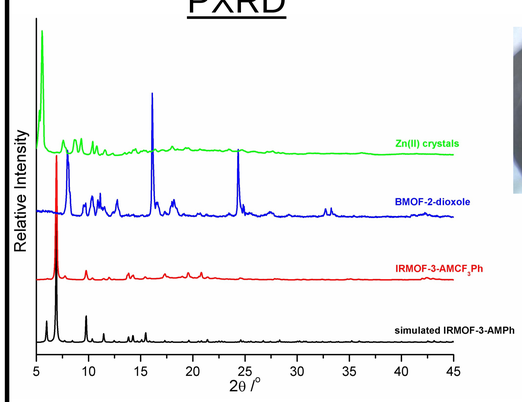


Zn(NO3)2.6H2O

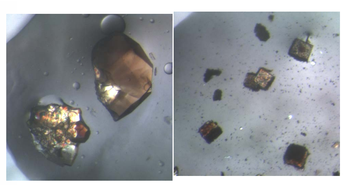
Experiment	Conditions	Observations
1	DMF 120 °C for 24 Hours	No crystals formed
2	DMF 35-100°C in 30 minutes, 100°C 24 hours 100-35 °C in 30 minutes	No crystals formed
3	DMF 120°C for 72 hours	Small white round crystals formed
4	DEF 120°C for 48 hours	Turned red; precipitate formed

Target Results

PXRD

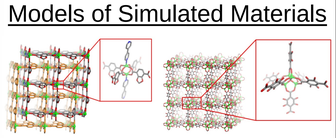


Microscope Images



Zn(II) crystals IRMOF-3-AMCF$_3$Ph

Models of Simulated Materials



Simulated IRMOF-3-AMPh BMOF-2-dioxole

Conclusions

- CF_3 functionalized ligand is synthesized, but CN functionalized ligand is not obtained.
- We attempt to incorporate the CF_3 functionalized ligand into three different types of MOFs. However, only two attempts yield crystals.
- Only the IRMOF-3-AMCF$_3$Ph is achieved, and the structure of IRMOF-3-AMCF$_3$Ph is confirmed by PXRD .

Acknowledgements

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•UCSD.