Ultrafast Synthesis of Metal Organic Framework (MOF) Critical for New CO_2 Uptake Technology

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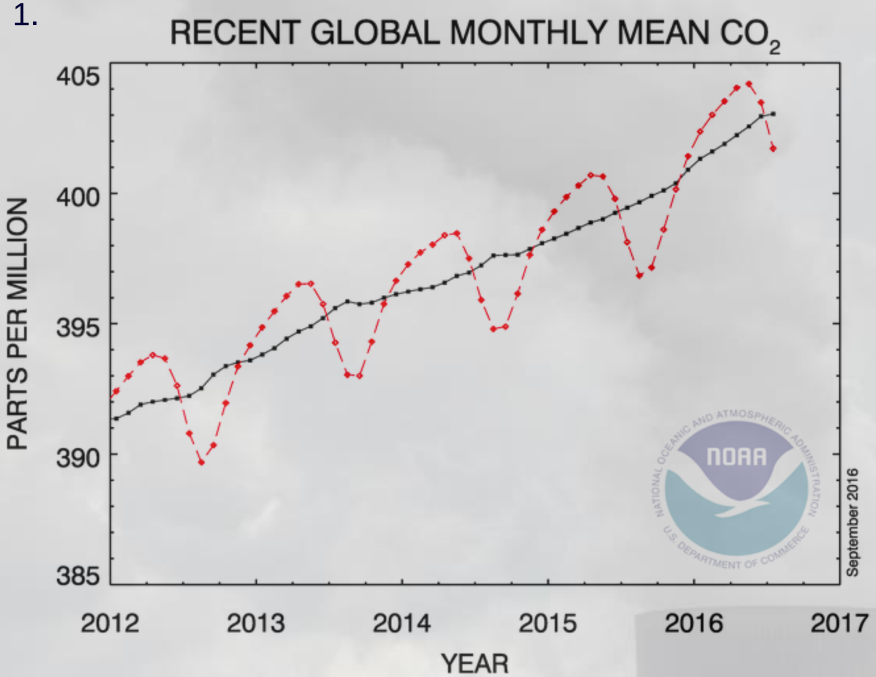
MOLECULAR FOUNDRY

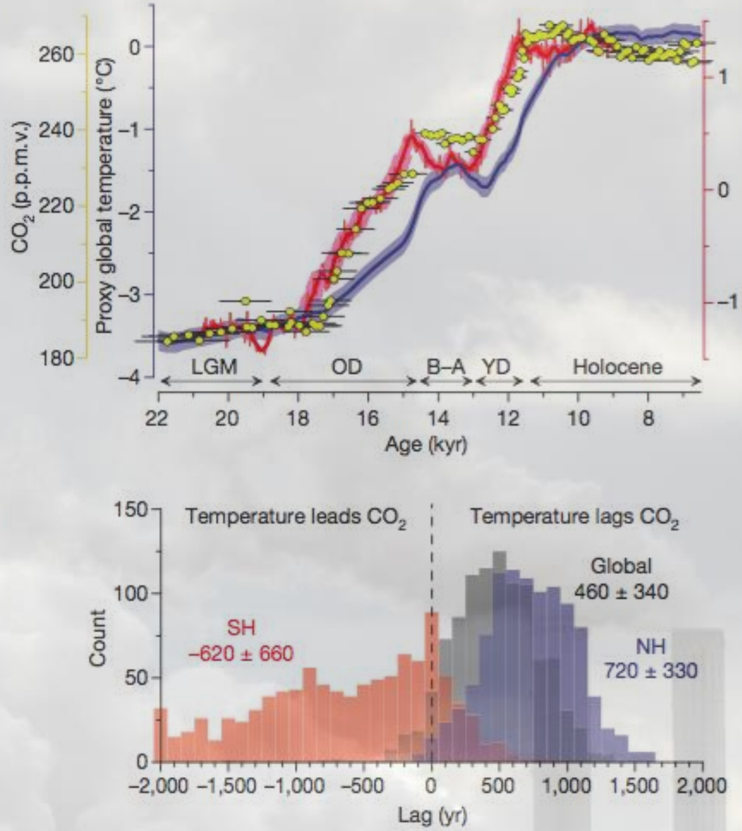
Increase of atmospheric CO_2 level and correlation with the global temperature

1.



In the last 10 years, atmospheric CO_2 increased by 2.1 ppm/year, rising 2 times faster with respect to 1960s

2.



CO_2 concentration leads the global temperature (96% accuracy)

1. http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html accessed September 18, 2016
2. Shakun, J. D. *et al.* Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation. *Nature* **484,** 49–54 (2012)

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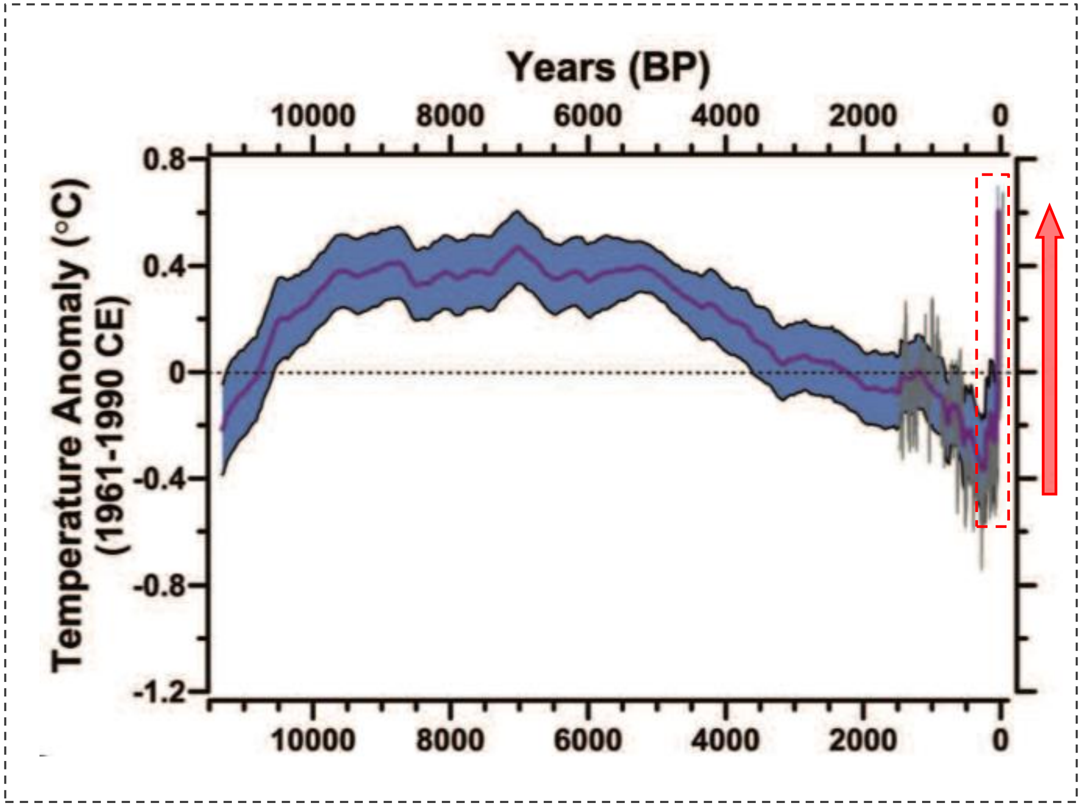
The global temperature trend

Last century abrupt discontinuity in temperature trend is strongly correlated to anthropogenic CO_2 emissions



Marcott, S. A., Shakun, J. D., Clark, P. U. & Mix, A. C. A Reconstruction of Regional and Global Temperature for the Past 11,300 Years. Science 339, 1198 (2013)

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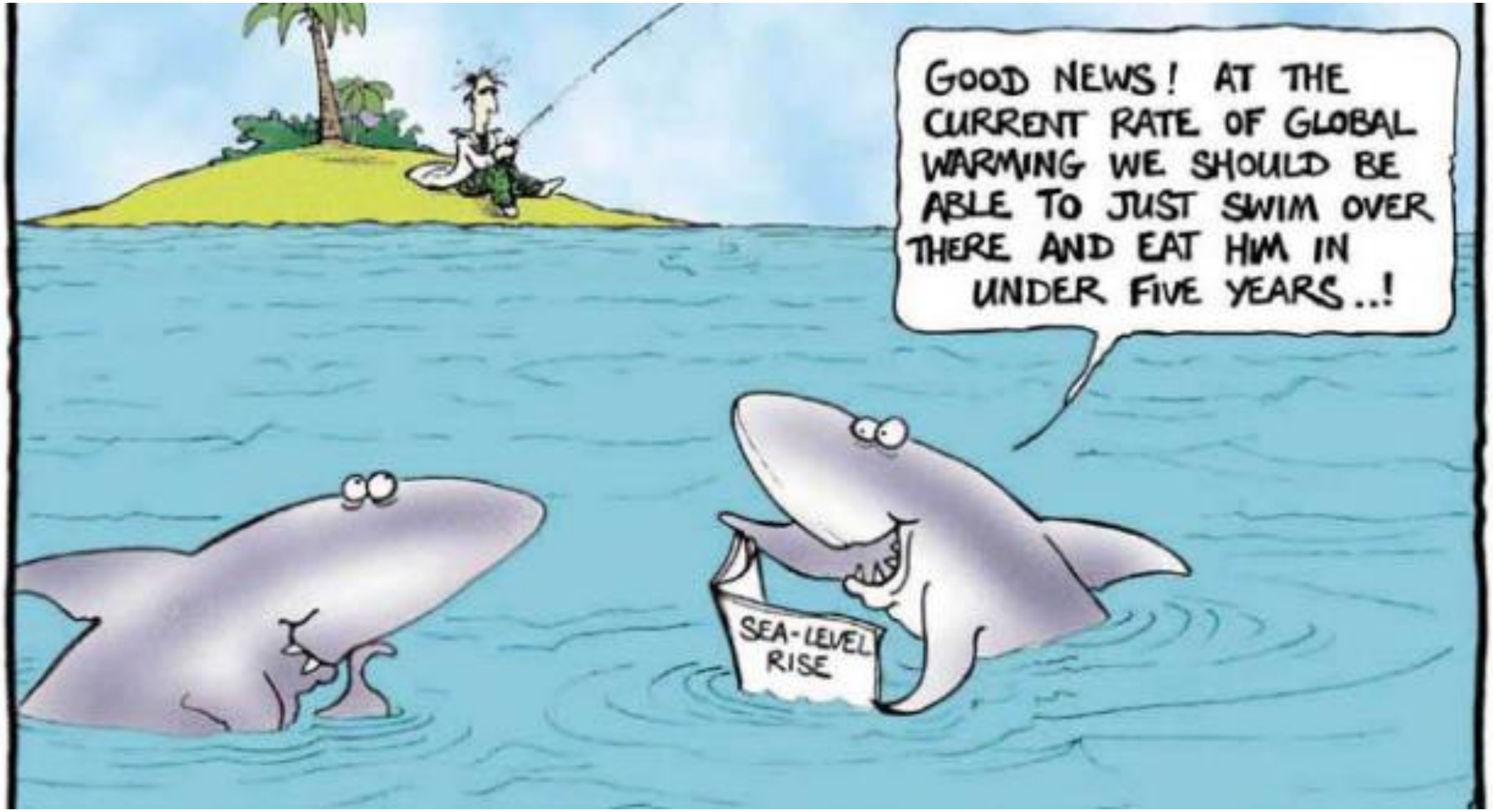
The cost of temperature rise



http://www.lab-initio.com

Revesz, R. L. et al. Global warming: Improve economic models of climate change. Nature 508, 173–5 (2014)

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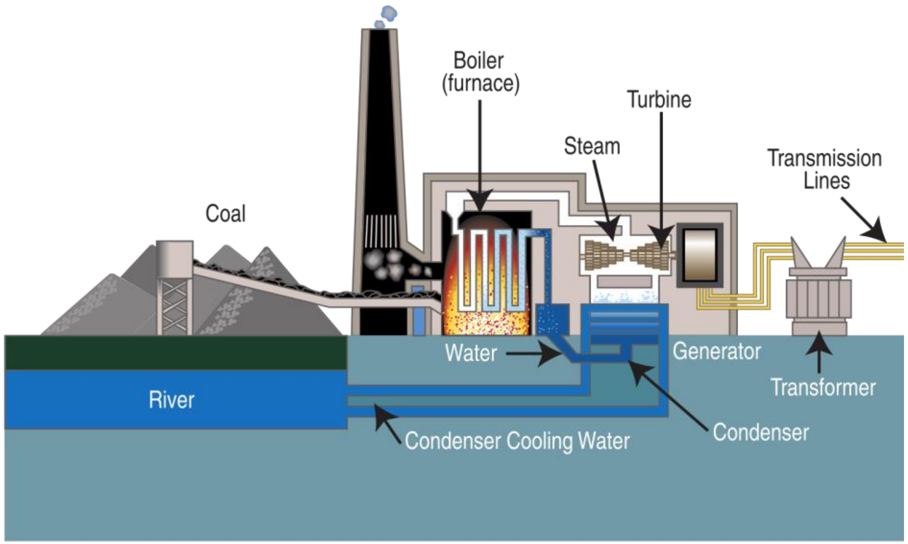
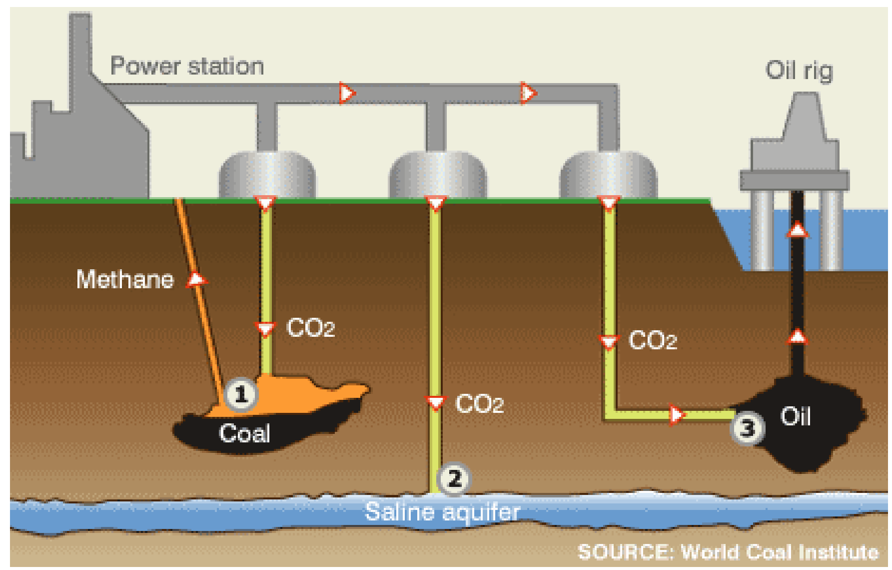
Solution: CO_2 capture and storage

The goal is to capture CO_2 at large point sources (fossil fuel power plants) and store it safely underground



http://upload.wikimedia.org/wikipedia/commons/4/4a/Coal_fired_power_plant_diagram.svg



http://news.bbc.co.uk/2/hi/science/nature/4468076.stm

IPCC special report on Carbon Dioxide Capture and Storage (2005)

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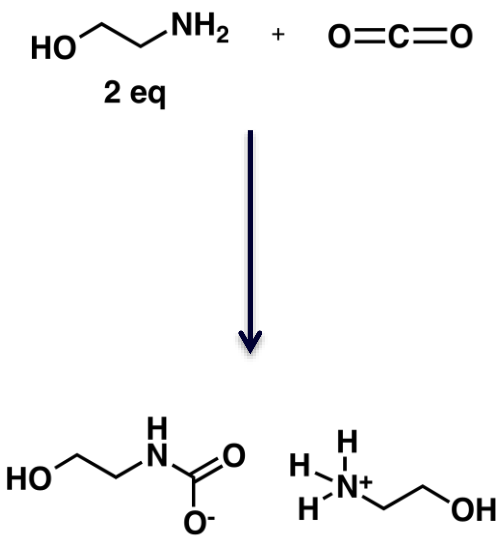
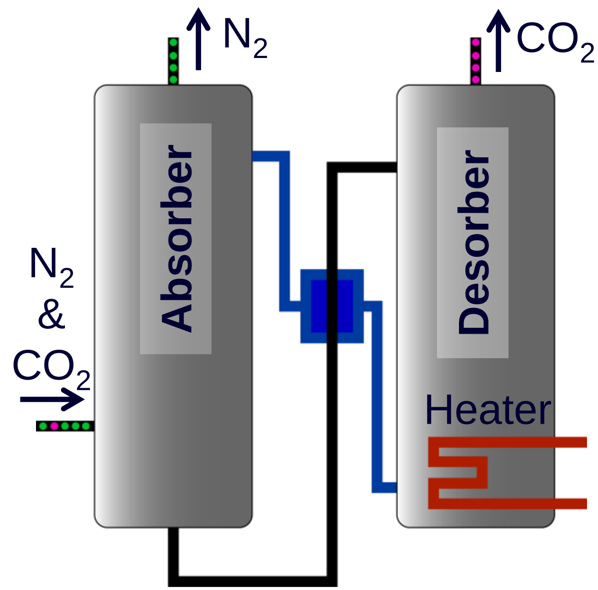
CO_2 capture: a regenerative approach

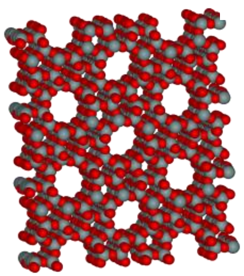
Amine scrubbing



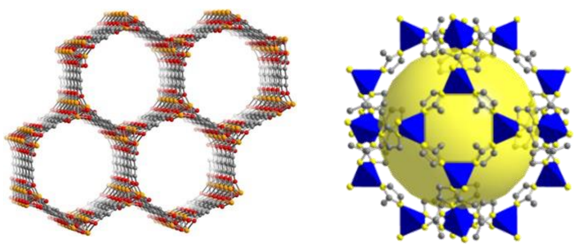


Porous Crystals

Zeolites



Metal-organic frameworks (MOFs)



- Easy to implement
- High CO_2 selectivity
- Decreases power plant output by **30%**

- Low energy consumption
- Gas adsorption tunability
- Low selectivity

Smit, B., Reimer, J., Oldenburg, C., Bourg, I. Introduction to Carbon Capture and Sequestration, Imperial College Press: London (2014)

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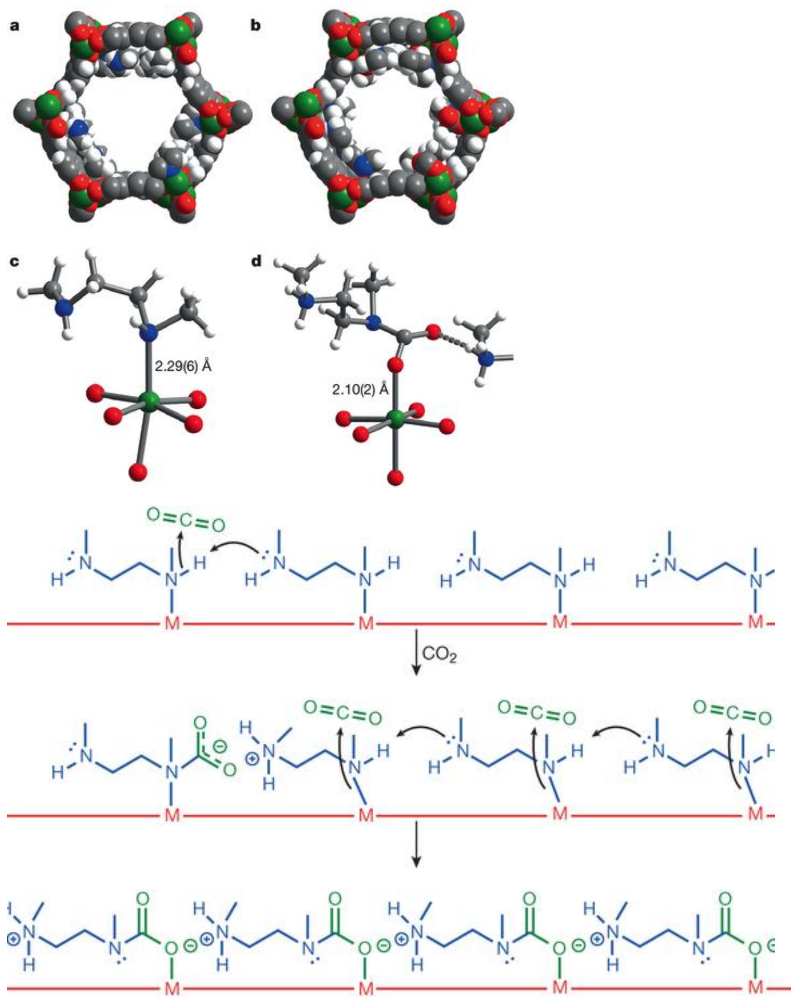
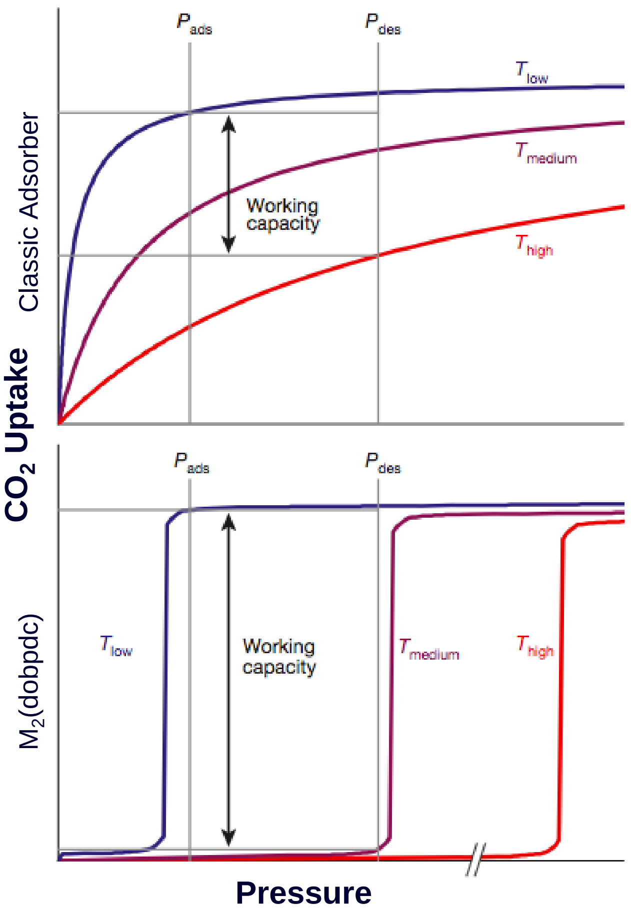
Combining amines with MOFs

Amines-appended phase-change M_2(dobpdc), for efficient CO_2 scrubbing





McDonald, T. M. et al. Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks. Nature 519, 303–8 (2015)

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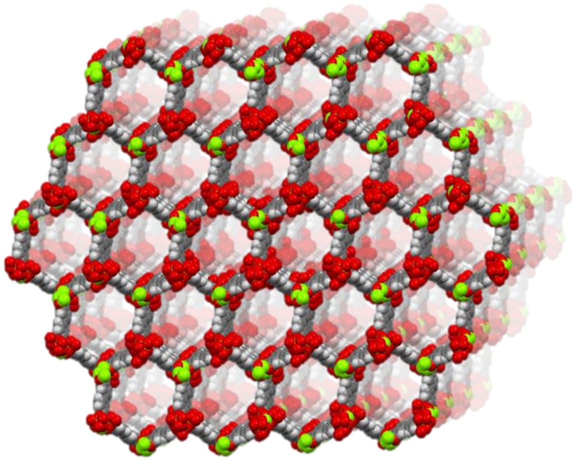
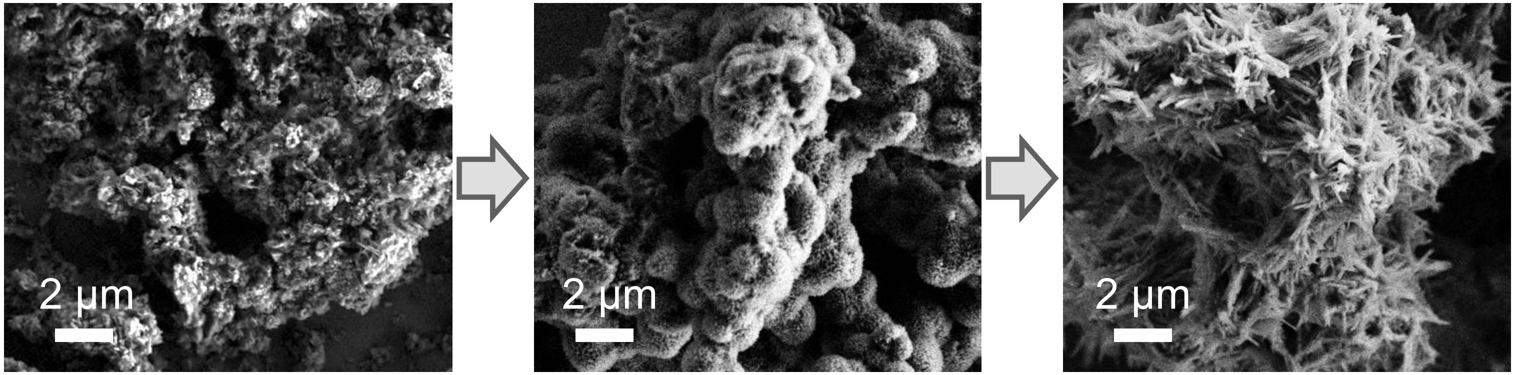
Motivations to our experiment

1. Quick synthesis of M_2(dobpdc) for efficient CO_2 scrubbing



2. Understanding metal oxide dissolution-crystallization to MOF



Maserati, L., Meckler, S. M., Li, C. & Helms, B. A. Minute-MOFs: Ultrafast Synthesis of M_2(dobpdc) Metal–Organic Frameworks from Divalent Metal Oxide Colloidal Nanocrystals. *Chem. Mater.* **28,** 1581–1588 (2016)

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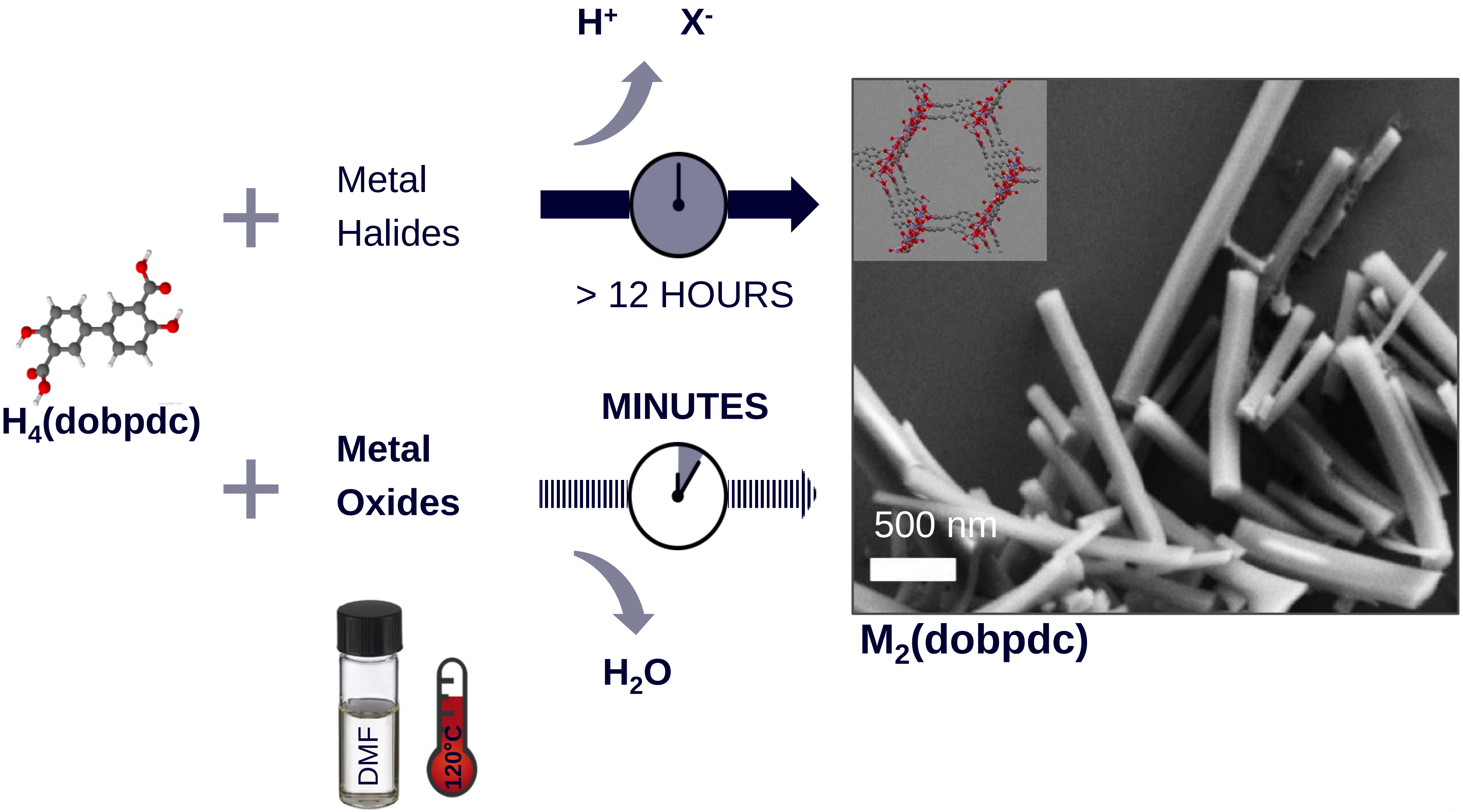
Experimental outline

Divalent Metal Oxides (MO) substitute molecular precursors, reducing the required time for MOF crystallization from 12 hours to minutes



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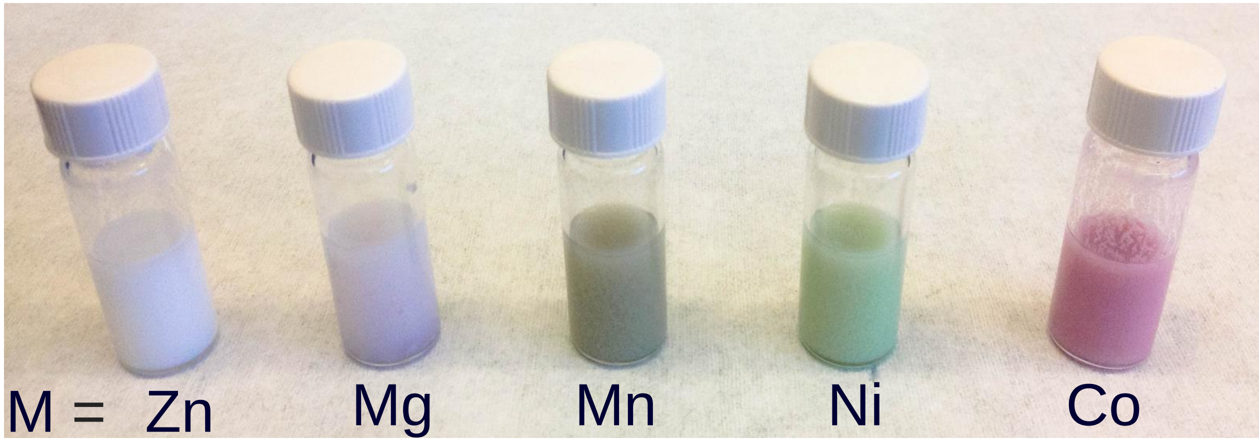
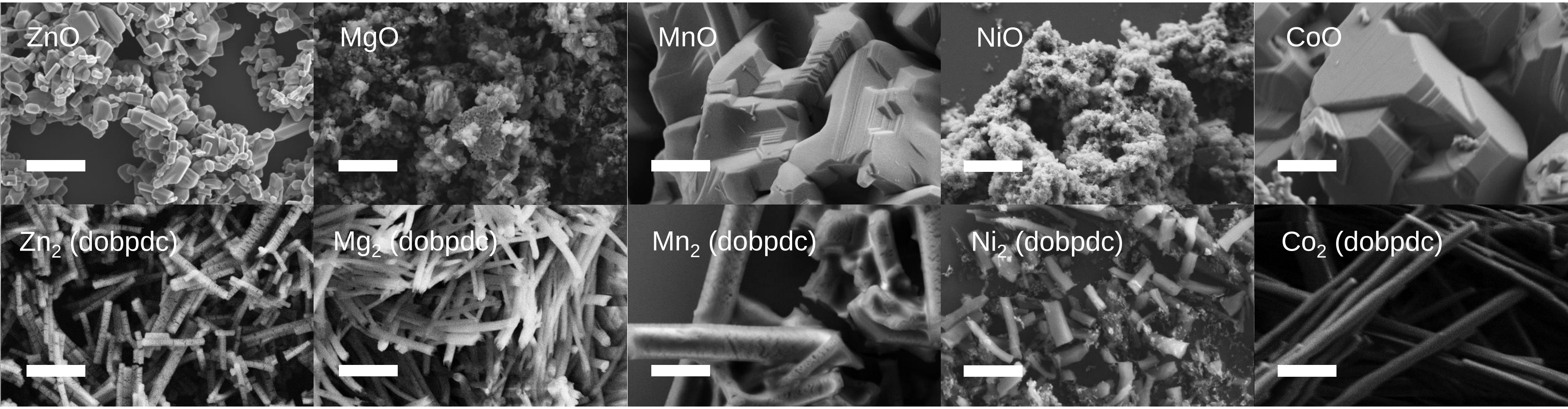
Synthesis results

M_2(dobpdc) produced from metal oxides precursors





Scale bars are 1μm

- The M_2(dobpdc) rod-shaped morphology is similar for all the different metals
- Precursors chemistry and morphology affect the reaction time

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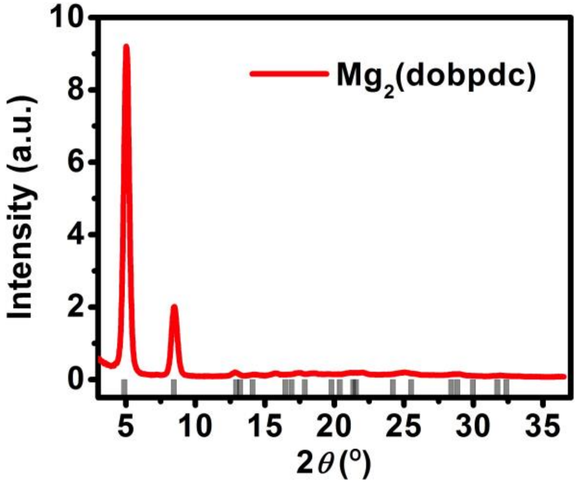
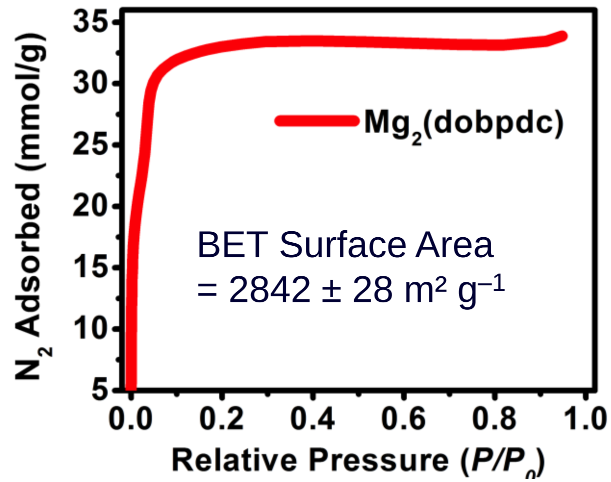
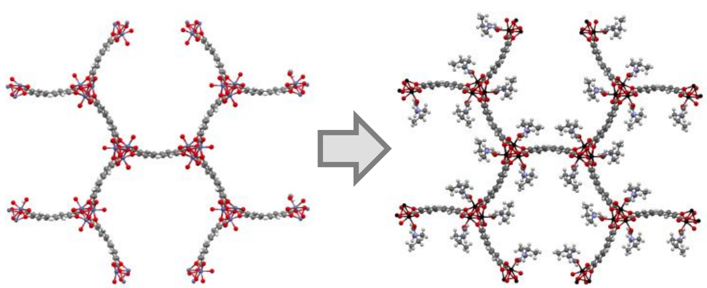
M_2(dobpdc) characterization

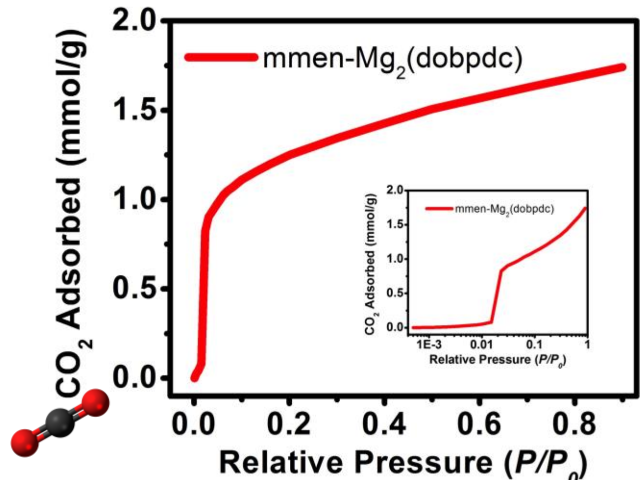
XRD and BET surface area confirmed high-quality materials; here the magnesium case is shown





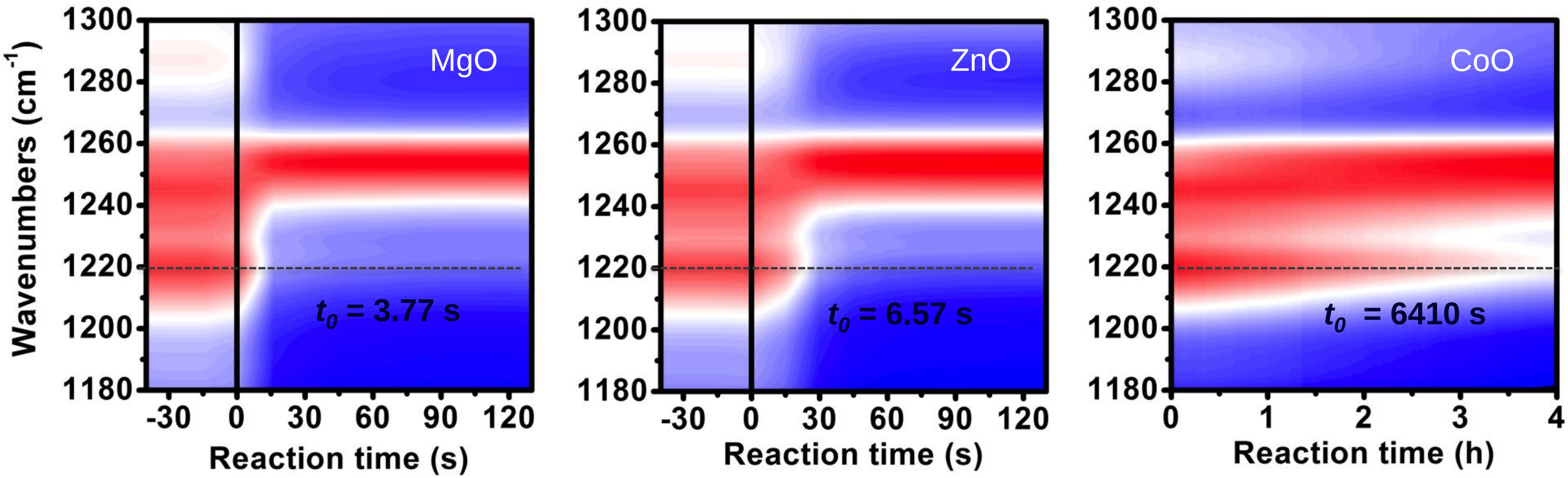
N,N'-dimethylethylenediamine (mmen) grafting

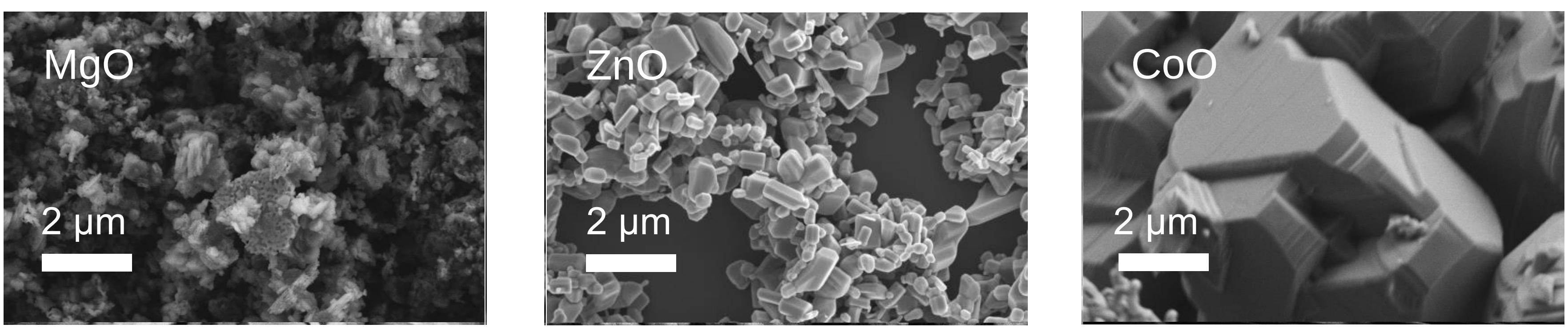




MO dissolution kinetics: M-comparison

In situ FTIR over time of the organic ligand reaction with metal oxides





In situ FTIR data fitting following: $log\,(f/(1-f)) = k\,(t - t_0)^{\dagger}$; $t_0 = 1/k$

† E. G. Prout and F. C. Tompkins, Trans. Faraday Soc., 1944, 40, 488–498.

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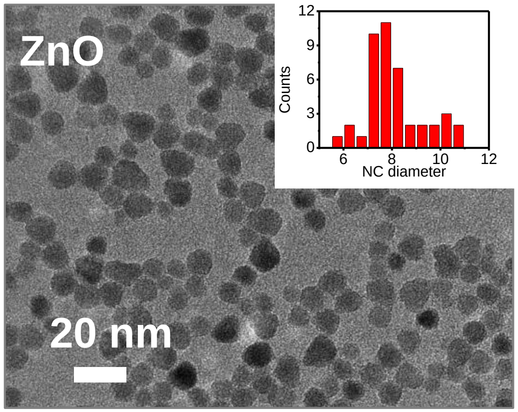
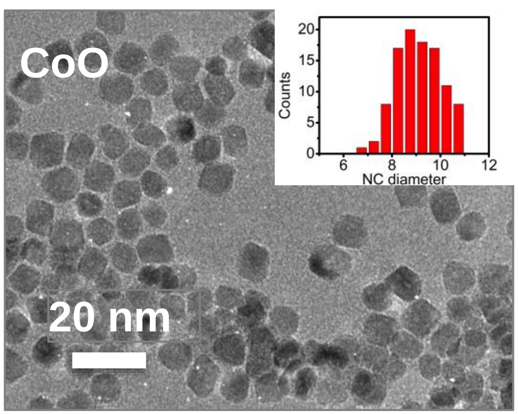
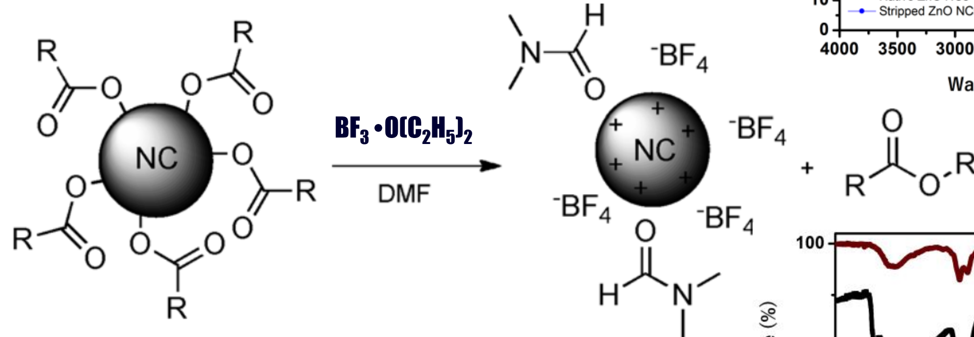
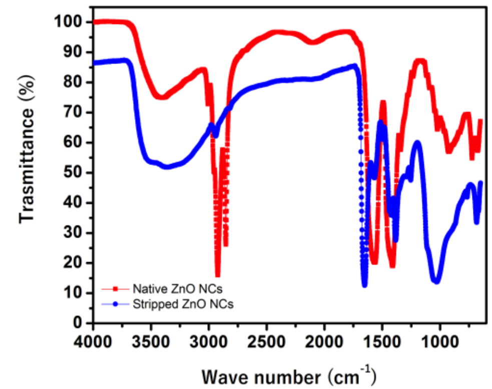
Pushing dissolution kinetics to the limit

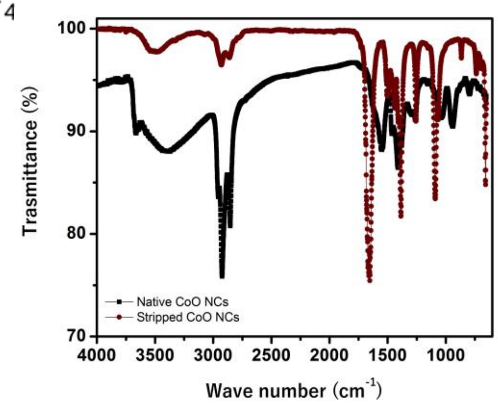
Ligand-stripped colloidal metal-oxide nanocrystals were used as precursors











Doris, S. E.; Lynch, J. J.; Li, C. Y.; Wills, A. W.; Urban, J. J.; Helms, B. A. *J. Am. Chem. Soc.* **2014**, *136*, 15702

Li, Y.; Afzaal, M.; O'Brien, P. *J. Mater. Chem.* **2006**, *16*, 2175–2180

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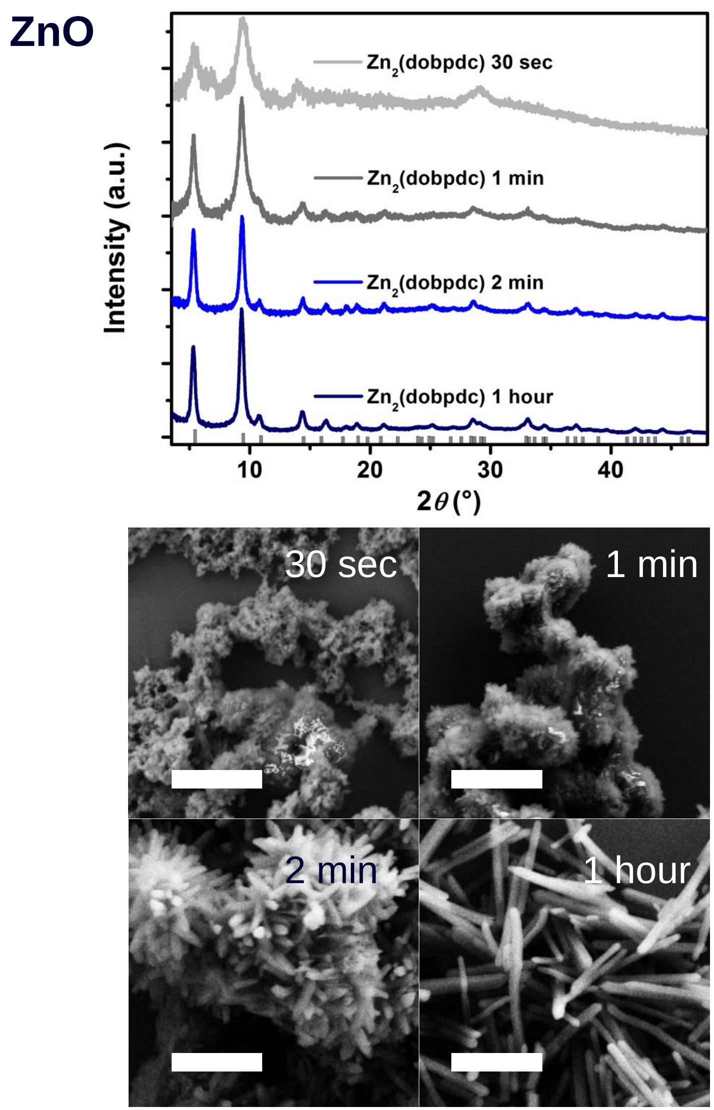
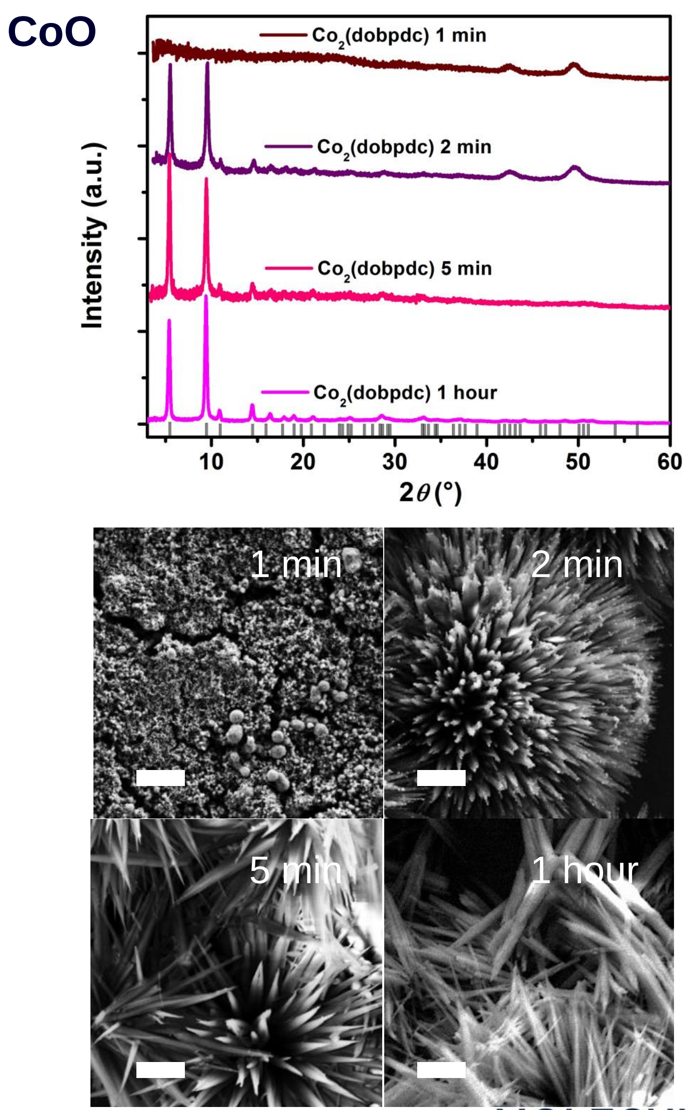
Minute-MOFs from MO Nanocrystals



Scale bars are 1μm



Scale bars are 1μm

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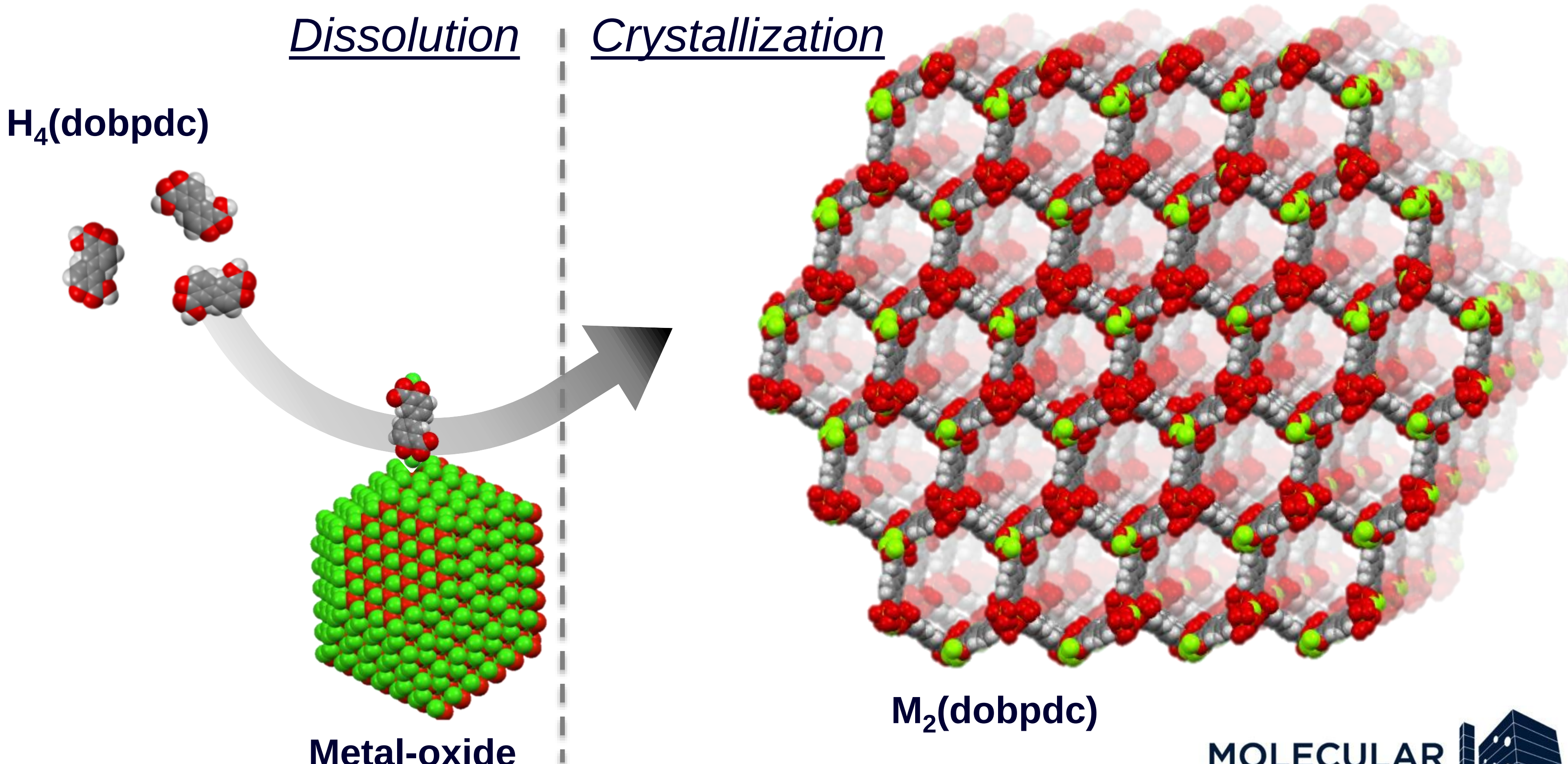
Conclusion

1. Metal oxides can be used as cheap and fast-reacting precursors for making M_2(dobpdc).

2. The metal-oxide dissolution is the rate-limiting factor. Therefore, nano-sized metal oxides push the synthesis of M_2(dobpdc) to its kinetic limit.



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- Wendy Queen
- Thomas McDonald
- Virginia Altoe