Controlling the Crystallite Size Distribution of Metal Organic Frameworks (MOFs) Using Base-Mediated Equilibrium Dynamics

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Primary CNF Tools Used: Dynamic Light Scattering: Malvern Nano ZS Zetasizer and Malvern NS300 NanoSight

Abstract:

Metal-organic frameworks (MOFs) are crystalline, porous materials with potential applications ranging from gas separations to catalysis. However, the synthesis of MOFs remains a "black box" — which makes it challenging to prepare frameworks with controlled crystallite size distributions. Generally, MOFs are prepared from the conjugate acid of the organic "linker" combined with a metal precursor and a source of base to deprotonate the acid. This is most commonly achieved using the decomposition of the solvent N,N-dimethylformamide (DMF). However, we hypothesized that the slow addition of base could instead be achieved simply by adding base slowly via syringe pump to a reaction mixture.

We have found indeed that the crystallinity of MOFs, specifically the framework Zn-MOF-74, can be improved by adding organic base slowly to the reaction mixture (Figures 1 and 2).

Summary of Research:

The improvement in crystallinity could be observed by powder X-ray diffraction and scanning electron microscopy (not shown). We attempted to further support our findings using the dynamic light scattering (DLS) instruments available at CNF, specifically the Malvern Nano ZS Zetasizer. However, the prepared MOFs were found to form unstable colloids in all tested media (including water and organic solvents), and thus did not yield meaningful data despite numerous attempts (Figure 3).

Unfortunately, the MOFs were also found to rapidly settle from solution, which also negatively impacted the DLS measurements. As such, we have abandoned DLS measurements at CNF for the time being.

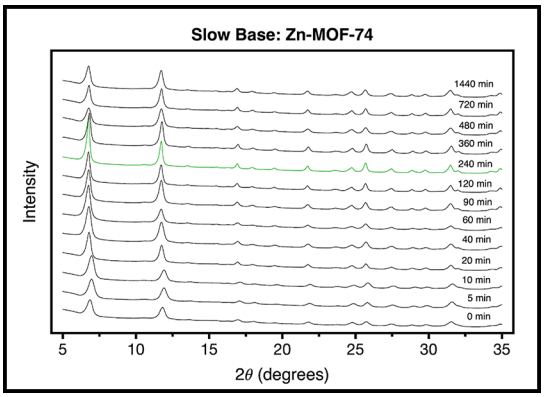

Figure 1: Powder X-ray diffraction patterns of Zn-MOF-74 prepared at a range of base addition times.

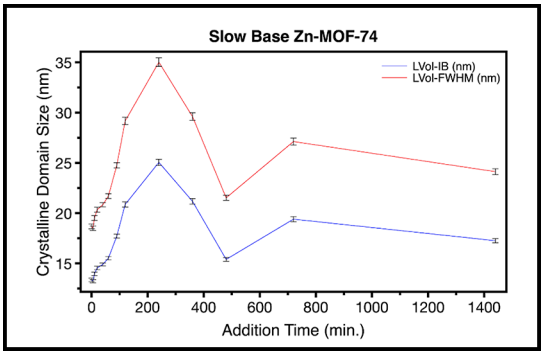

Figure 2: Average crystalline domain sizes of Zn-MOF-74 crystallites prepared by slow addition of base.

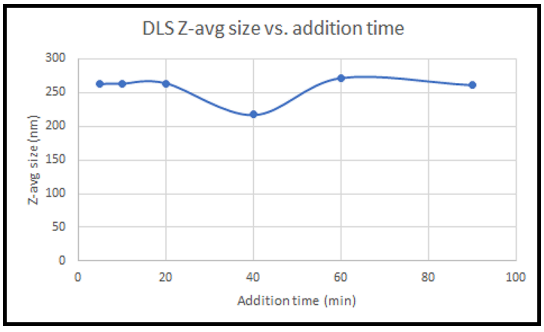

Figure 3: Attempted DLS measurements of MOFs, which yielded unmeaningful results.