Exploring Polymorphism in Flexible Disulfide-Linked Metal-Organic Frameworks

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Introduction

Metal-Organic Frameworks (MOFs) are a family of coordination polymers consisting of inorganic metal centers which coordinate to organic linkers resulting in the formation of highly ordered, 3-dimensional, crystalline networks[1]. MOFs form through a mechanism of self-assembly due to their building unit's solubility and reversible organometallic interactions typically involving oxygen (commonly a carboxylate group) or nitrogen (in the form of a pyridyl ring).

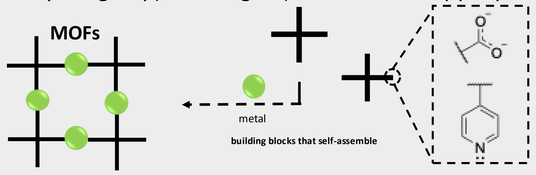

Figure 1: *an illustration of MOF self-assembly and common organic linker motifs.*

Traditional MOF syntheses rely on highly rigid organic linkers to provide predictable crystallinity and architectural properties. More recently, flexible linkers have been incorporated providing conformational differences in crystal formation and porosity[2]. This unique property allows researchers to observe unique coordination patterns without altering building units on the molecular level. Disulfide containing linkers provide this level of flexibility while also adding a layer of redox responsiveness, which can have applications to both drug delivery and chemotherapy[3].

Here, we report two unique MOF characterizations using 4,4'-dithiobenzoic acid (4-DBA) and Zinc Acetate ($Zn(CH_3COO)_2$). These two structures referred to as Zn-MOF-α and Zn-MOF-β, form under varying solvent conditions[4]. Notably, the addition of water into the solvent system leads to the prevailing of the β conformation. **Using micro electron diffraction (micro-ED) derived packing units, along with powder X-Ray Diffraction (PXRD) and Scanning Electron Microscopy (SEM) these two crystal pathways can be observed and studied.**

Experimental Methods

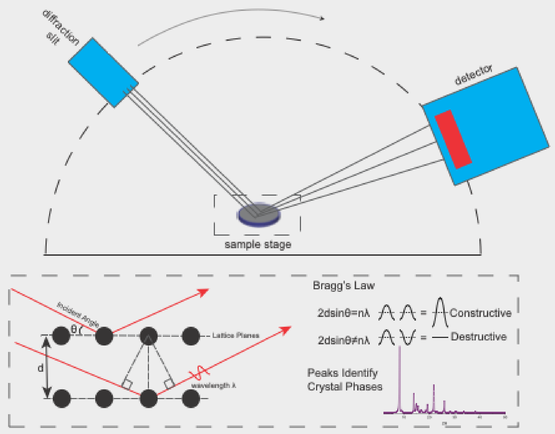

Figure 2: *An illustration showcasing the mechanism of PXRD and how a crystal pattern is derived.*

Molecular Design

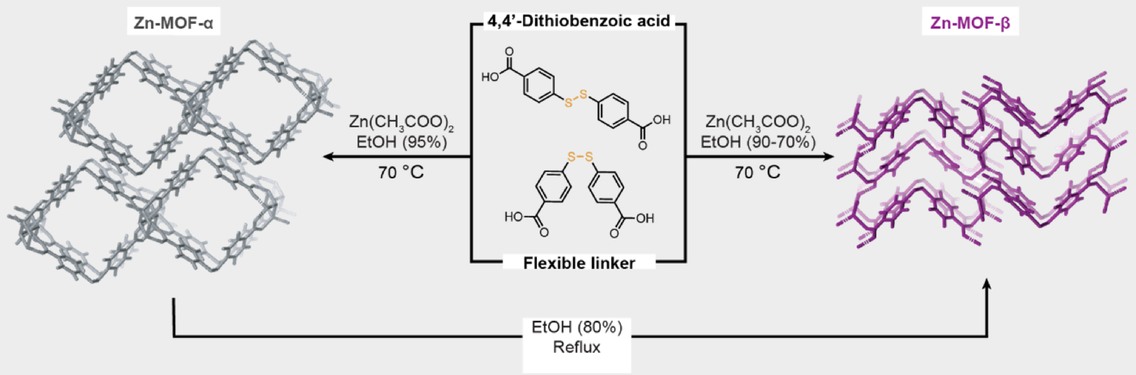

Figure 3: *Molecular design of the two unique crystalline pathways and their synthetic routes. 3-dimensional representation derived from micro-ED data.*

Scanning and Transmission Electron Microscopy (SEM, TEM)

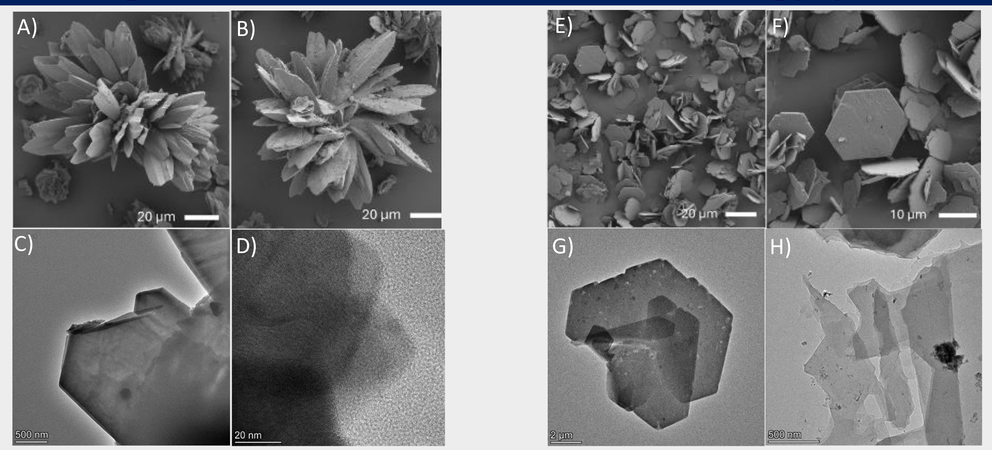

Figure 4: *SEM and TEM images showing the morphological structure of Zn-MOF-α (A-D) and Zn-MOF-β (E-H) showcasing their unique particle shaping.*

Powder X-Ray Diffraction (PXRD)

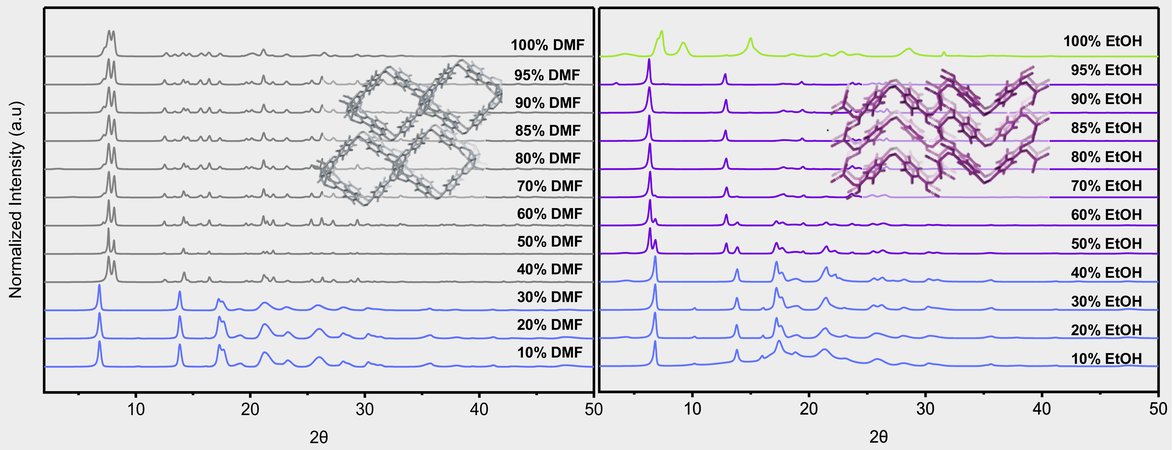

Figure 5: *Normalized and Y offset PXRD patterns of MOF formation using two different solvent systems in water. An increase of DMF concentration results in α conformation while EtOH favors the β state.*

Alternative Directions

The data from the PXRD patterns show us a shift in crystallinity with the addition of water into the solvent system. It remains difficult to say whether water is altering the flexibility of the disulfide bond, or if it is having impacts on the coordination sphere itself. A way we can further explore this is by exchanging the flexible linker with a rigid alternative. Using a linker synthesized via a Sonigashira cross-coupling, a linker with a locked linear conformation can be used with identical MOF formation conditions. The resulting PXRD patters would provide valuable insight into water's role in affecting the current molecular designs coordination environment.

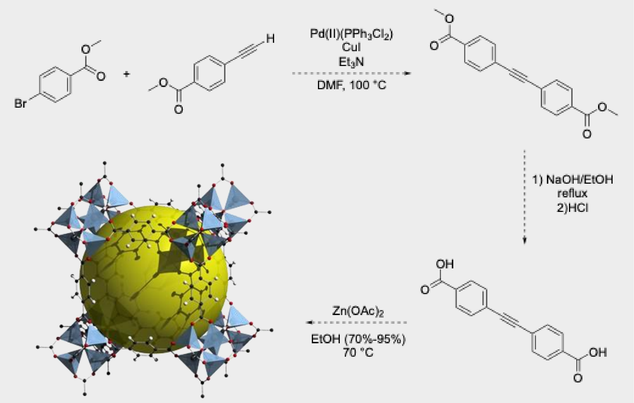

Figure 6: *Schematic of the proposed rigid linker synthesis and MOF formation conditions.*

In addition to the fundamental studies of flexible MOF Formation, more applied studies can be undertaken to reduce the crystal particle sizing. Reducing particles down to the nanoscale would allow the flexible framework to be considered for drug delivery applications, which was the original intent for this material.

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