

Scalable Defect Engineering in Metal-Organic Frameworks via High-Concentration Self-Assembly Utilizing Pre-Assembled Cluster Precursors

CNF Project Number: 2996-21

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Primary Source(s) of Research Funding: National Institute of General Medical Sciences of the National Institutes of Health under award number R35GM138165

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Primary CNF Tools Used: Rame-Hart 500 Goniometer

Abstract:

Metal-organic frameworks (MOFs) are a class of porous, crystalline materials that can have tailored properties based on the incorporation of defects and are promising for applications in gas storage, catalysis, and separations. Syntheses of MOFs on large scale, however, remain a major roadblock to their further implementation, as many are synthesized using solvothermal methods under highly dilute (≤ 0.01 M) conditions. Additionally, a large excess (>50 equiv.) of competing acid modulators is often used to enhance the crystallinity of and the number of defects in the resulting MOF, further amplifying the associated waste of MOF synthesis. We demonstrated that zirconium and hafnium MOFs are generally able to be synthesized at much higher reaction concentrations (up to 1.0 M). Additionally, the use of pivalate-capped metal cluster precursors — as opposed to a standard metal chloride salt — led to the inclusion of pivalate defects at missing-linker sites, which increased the hydrophobicity of the resulting MOF. Our findings provide a user-friendly approach to the scalable synthesis of defect engineered MOFs by drastically reducing solvent and acid modulator waste.

Summary of Research:

Metal-organic frameworks (MOFs) are crystalline, porous solids constructed from inorganic nodes bridged by organic linkers [1]. MOFs are promising for a variety of applications, including heterogeneous catalysis, gas storage, and chemical separations, due to their highly tunable pores that can resist collapse upon desolvation [1]. The controlled incorporation of defects in MOFs, such as missing-linker defects, can be utilized to tune the resulting framework properties by further modifying the size and chemical functionality of the pores [2]. Despite their potential, a major challenge to the further development of MOFs is their synthesis on bench top

scales (1-100g). This is mostly due to the excessive waste generated during synthesis as many use very dilute (~ 0.01 M) solvothermal conditions in hazardous solvents such as dimethylformamide (DMF) [3]. Additionally, many syntheses use a staggering excess (>50 equiv.) of competing acid modulators to enhance the crystallinity of and to increase the number of defects in the resulting MOFs [1]. These synthetic challenges are exemplified by frameworks composed of zirconium (Zr) and hafnium (Hf) cluster nodes, such as UiO-66 (UiO = Universitetet i Oslo) (Figure 1). Zr- and Hf-MOFs display exceptional tunability, hydrolytic stability, and robust structures that can accommodate large amounts of defects but often require dilute synthesis conditions and large amounts of modulators to yield crystalline products [1].

Recently, we reported that Zr- and Hf-MOFs can generally be self-assembled at much higher reaction concentrations (up to 1.0 M) than traditionally utilized [4]. By simply combining stoichiometric amounts of terephthalic acid (H_2bdc) linker and $ZrCl_4$ in DMF at concentrations up to 1.0 M, crystalline UiO-66 (labeled UiO-66-1.0M ($ZrCl_4$)) was obtained (Figure 2). Likewise, a pivalate-capped Zr_6 cluster ($ZrPiv$) could be combined with stoichiometric H_2bdc and hydrochloric acid (HCl) — to promote ligand exchange of pivalates for linkers — to yield crystalline MOF labeled UiO-66-1.0M ($ZrPiv$) (Figure 2). These high-concentration samples displayed similar crystallinity to a dilute prepared sample and had Brunauer-Emmett-Teller (BET) surface areas comparable to literature values [4]. A key difference, however, was that UiO-66-1.0M ($ZrPiv$) contained pivalate ligands as linker substitution defects. Proton nuclear magnetic resonance (1H NMR) analysis was used to determine a pivalate:linker ratio of 0.11:1, which is comparable to reported dilute syntheses of UiO-66 that use a slight excess of competing carboxylic acid modulators. Additionally, this ratio was higher than for a

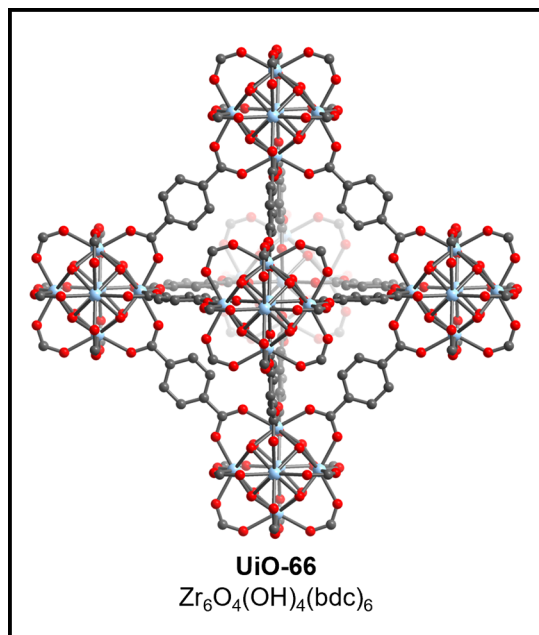


Figure 1: The structure of UiO-66. Gray, red, and light blue spheres represent carbon, oxygen, and zirconium, respectively. Hydrogens are omitted for clarity.

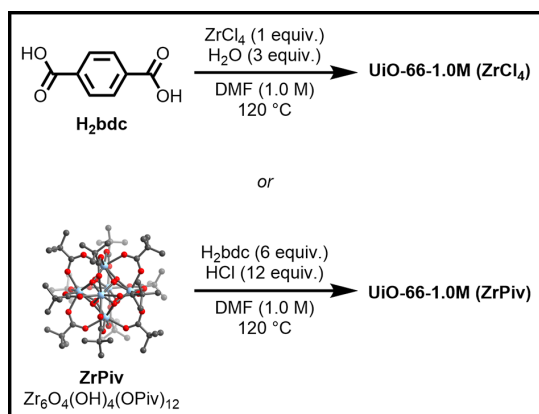


Figure 2: High-concentration synthesis of UiO-66 from either $ZrCl_4$ or ZrPiv. Adapted with permission from ref [4]. Copyright 2023 American Chemical Society.

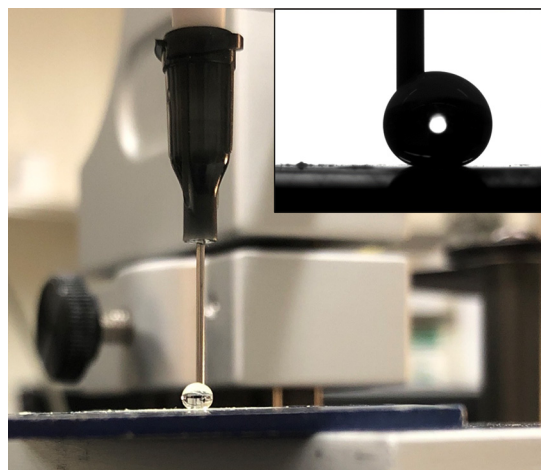


Figure 3: Photo of a water drop on UiO-66-1.0M (ZrPiv) powder. Inset: water contact angle of UiO-66-1.0M (ZrPiv). Adapted with permission from ref [4]. Copyright 2023 American Chemical Society.

sample prepared at high concentrations using $ZrCl_4$ and the same amount of pivalic acid present in ZrPiv [4]. Thus, using ZrPiv as a precursor is more effective at carboxylate defect incorporation than traditional acid modulation in high-concentration syntheses.

We hypothesized that UiO-66-1.0M (ZrPiv) should have enhanced hydrophobicity due to the inclusion of nonpolar pivalate defects. When water is added to the pivalate containing MOF, it beads up indicating that the material has a hydrophobic surface (Figure 3). Water contact angle measurements determined that UiO-66-1.0M (ZrPiv) had a large contact angle of 162° (Figure 3 inset), which indicates this as a super-hydrophobic surface [4].

Additionally, UiO-66-1.0M (ZrPiv) floats on water whereas UiO-66-1.0M ($ZrCl_4$) is rapidly wetted and sinks (Figure 4 inset). Water vapor adsorption isotherms were also measured to further probe if the interior pore surface of the pivalate containing MOF showed enhanced hydrophobicity (Figure 4). The relative pressure at which half of the total water capacity is reached (α) is larger for UiO-66-1.0M (ZrPiv) ($\alpha = 0.30$) indicating that its pore surface has weaker interactions with adsorbed water than UiO-66-1.0M ($ZrCl_4$) ($\alpha = 0.24$) [4]. Overall, these results demonstrate that preformed cluster precursors can effectively install property altering defects and thus enable defect engineering in user-friendly high-concentration MOF synthesis.

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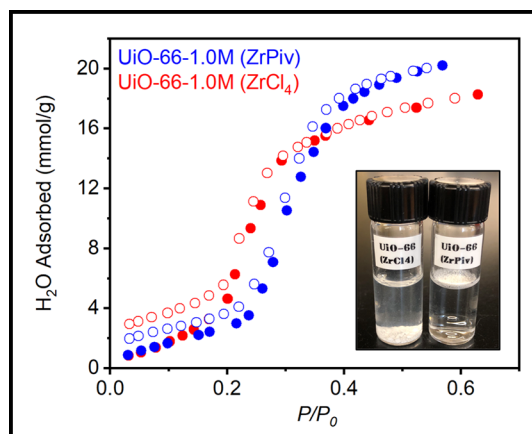


Figure 4: Water vapor adsorption isotherms of high-concentration UiO-66 samples. Inset: UiO-66-1.0M (ZrPiv) (right) floating on water vs. UiO-66-1.0M ($ZrCl_4$) (left) sinking in water. Adapted with permission from ref [4]. Copyright 2023 ACS.