Stabilizing defects in metal-organic frameworks: Pendant Lewis basic sites as capping agents in UiO-66-type MOFs toward highly stable and defective porous materials

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Lend me a hand! Pendant ether groups stabilize Zr-MOFs with significant ligand defects (~50%) through capping open metal sites.¹

Implications in preparation of materials with disordered mesopores, improving stability, and introducing synergistic functionality.

Abstract

An isostructural series of zirconium-based metal-organic frameworks (ZrMOFs) with UiO-66-type structure (including three previously unreported materials) have been successfully synthesized from combination of mono- and di-substituted terephthalic acids and ZrCl_4 . Sterically demanding pendant groups with Lewis basic sites are found to impart significant defects within the crystal structure while simultaneously stabilizing the MOFs toward water, acid, and base, permitting access to materials with disordered mesopores. Furthermore, comparably sized pendant group with no Lewis basic sites results in formation of amorphous material. The materials have also been investigated as sorbents for removal of trace heavy metals from acidic aqueous solutions, with thiol- and sulfide-containing materials exhibiting significant potential in removal of Hg^{2+} and Ag^+ .

Background and Objectives

Figure 1 a) Preparation of UiO-66-type MOFs from $\text{H}_2\text{BDC-R}$. b) Metal and ligand SBU in pristine UiO-66. c) UiO-66 SBU with ligand defect site highlighted.²

MOFs in the UiO-66 family are of the formula $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC-R})_n \cdot xS$, BDC^{2-} = benzene dicarboxylate (terephthalate), S = solvent. The Zr-SBU (secondary building unit) coordinates 12 carboxylates (six BDC-R^{2-} ligands) in the pristine, non-defective, form ($n = 6$).

It is well-known, however, that UiO-66-type MOFs can be prepared with varying numbers of ligand defects, even for the same MOF. For example, varying reaction conditions for the parent MOF of the series, UiO-66, can result in a varying number of ligand defects introduced, typically 1-3 of the 12 carboxylates ($n = 4.5\text{--}5.5$).³⁻⁵ While introduction of defects can increase porosity, this often comes at a sacrifice to stability. To this end, we sought to introduce pendant functionalities that could serve as stabilizing entities to prepare water-stable functional materials for scavenging of heavy metal ions from acidic environments.

Since acid-mine drainage is a primary source of trace heavy metal contamination, the realization of *acid-stability* and *highly efficient metal uptake* was essential in preparing new materials.

Experimental Design and Results

A series of terephthalic acid derivatives were used to prepare UiO-66-type MOFs through combination of a solution of ZrCl_4 , dimethyl formamide (DMF), and modulating agent (concentrated acetic acid or hydrochloric acid), with a DMF solution of $\text{H}_2\text{BDC-R}$ in glass vial. The resultant solution was sealed with plastic screw cap and heated in programmable oven. Resultant crystalline solids were isolated via centrifugation, washed with DMF, and then washed with ethanol.

Figure 2 Ligand series used in the preparation of UiO-66-type MOFs in this study. *MOF not observed.

MOFs were first characterized via powder X-ray diffraction (PXRD) methods. As-synthesized MOFs were subjected to PXRD analysis after washing with ethanol and drying in air. The same PXRD analyses were performed for samples stirred in water for 24 h, in pH = 2 aqueous nitric acid for 24 h, and in pH = 12 aqueous potassium hydroxide for 24 h. PXRD analyses show that thioether functionalities serve to stabilize the MOFs to adverse conditions.

Thermogravimetric analyses (TGA) were conducted to determine numbers of ligands.⁶ High- and low-connectivity (H-C and L-C, respectively) estimates were provided when no clear plateau was observable for the “final” step in ligand combustion.

Figure 4 TGA curves for UiO-66-type MOFs (left) and example of mass differences in high- and low-connectivity (H-C and L-C, respectively) estimates. The table to the right provides select data from TGA curves used to determine numbers of ligand defects.

Nitrogen sorption isotherms show that UiO-66-2SEtSMe crystallizes as a *mesoporous material*, whereas the remainder of MOFs in initial series are microporous (left).

Trace heavy metal adsorption analyses were conducted by dispersing ~10 mg MOF in 10.00 mL solution (~7 ppm analyte), shaking for 3 h, isolating the solid by centrifugation, and evaluating via inductively-coupled plasma mass spectrometry. Selected data are shown in the table to the right. UiO-66-SMe shows promise for separation of Ag^+ from Hg^{2+} .

MOF	METAL	% METAL REMOVED
-2SH	Mercury	98%
-2SH	Lead	85%
-2SEtSMe	Silver	>99%
-SMe	Silver	98%
-SMe	Mercury	~0%

Identifying the Role of Pendant Group

To determine the role of pendant functionality in stabilizing highly defective UiO-66-type MOFs, the ligands $\text{H}_2\text{BDC-2OEtOMe}$ and $\text{H}_2\text{BDC-2OtBu}$ were prepared. Owing to their comparable steric bulk, we were able to directly determine the effects of the terminal (thio)ether functionalities on MOF stability and defect formation. Identical synthesis conditions as that used for UiO-66-2SEtSMe were employed, exchanging the ligand precursor with the -2OEtOMe and -2OtBu derivatives.

PXRD analyses (above) revealed that isostructural UiO-66-type MOF is obtained when employing the -2OEtOMe derivative, whereas the -2OtBu results only in amorphous powder. Furthermore, TGA indicates ~40% defects in UiO-66-2OEtOMe, comparable to that observed for its sulfur-containing counterpart.

Conclusions

We have shown that sterically hindering pendant functionalities can effectively introduce ligand defects into UiO-66-type MOFs. Furthermore, we show that such groups require pendant basic site capable of binding unsaturated Zr^{4+} sites to stabilize highly defective Zr-MOFs. These pendant (thio)ether sites substantially enhance stability toward acidic and basic aqueous conditions. Additionally, UiO-66-SMe proves a promising material for separation of Ag^+ from Hg^{2+} .

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