

Synthesis of Sulfonate-Containing Group 13 Metal–Organic Frameworks

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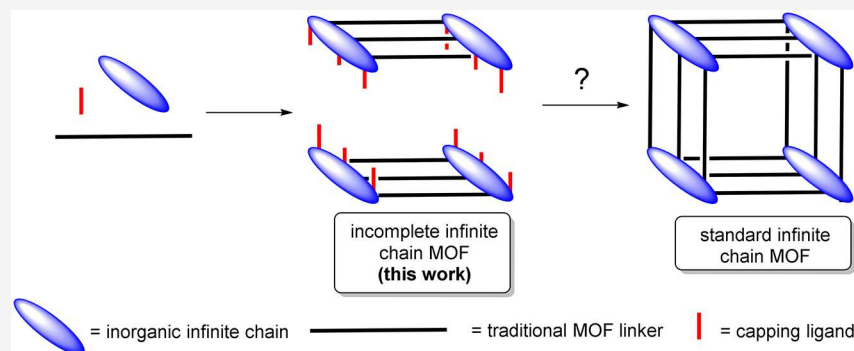
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ABSTRACT: The $[M(OH)(O_2CR)_2]_\infty$ infinite chain is a prevalent inorganic building unit in the construction of metal–organic frameworks (MOFs). Knowledge of its mechanism of formation enables the development of more efficient MOF syntheses that are required to advance the applications of these materials. To this end, identifying relevant intermediates is expected to enhance the mechanistic understanding of the formation of the infinite chain. Seeking to investigate the potential intermediary role of “incomplete infinite chains” in the formation of group 13 infinite chain MOFs, we employed linkers containing chelating functional groups to arrest self-assembly along a polymerizable axis. This resulted in the formation of four novel sulfonated frameworks comprised of incomplete infinite chains (YCM-61, -71, -72, and -73, YCM = Youngstown Crystalline Material). Notably, one of the frameworks (YCM-61) presents a solid-state Raman vibration bearing similarity to that previously ascribed to a MIL-53(Al) intermediate.

Metal–organic frameworks (MOFs) are a class of porous crystalline coordination polymers that are known for their diversity of structures and applications.¹ Despite the limitless possibilities of MOF architectures, privileged inorganic building units predominate, given their ease of synthesis and stability profiles. These inorganic building units include the Zn_4O cluster (IRMOF series),² Zr_6 cluster (UiO series),³ M_3O cluster (MIL-100 series),⁴ and the infinite chain (MIL-53),⁵ among others. Traditionally comprised of an octahedral +3 metal, four κ^1 -carboxylates, and two μ^2 -bridging OH groups, the $[M(OH)(O_2CR)_2]_\infty$ infinite chain is of great interest in MOF synthesis, as it can accommodate a plethora of metals.⁶ Consequently, MOFs with such infinite chains have been synthesized with Al,⁷ Ga,⁸ In,⁹ Fe(III),¹⁰ Cr(III),¹¹ Sc,^{12,13} and V(III, IV, III/IV).¹⁴ Specifically, MOFs containing Al-infinite chains are known for their stability and have potential in myriad applications.^{6,7,15} Thus, there is interest in studying the mechanism of Al-infinite chain MOF formation, notably that of MIL-53.

Distaso and Hartmann have spectroscopically identified a molecular intermediate formed during the self-assembly of MIL-53(Al) that they termed a “prenucleation building unit”

(PNBU). They observed a 780 cm^{-1} vibration in both solution-phase Raman and IR spectra and assigned it to a monomeric metal-linker complex with the proposed structure $[Al(H_2O)_4(CO_2R)]^{2+}$. Furthermore, they demonstrated that this PNBU is consumed in solution as the completed MIL-53(Al) infinite chain forms.^{16–18}

Previously, we have reported the synthesis of “intermediate-MOFs”, which we define as MOFs comprised of partially formed prominent inorganic building units.^{19–22} We hypothesize that these MOFs can form if the incomplete building units populate solution long enough to polymerize and self-assemble in such a way that a new MOF forms and the canonical structure cannot. The report of the Al-PNBU inspired us to explore the possibility of synthesizing incomplete group 13 infinite chains and investigate their relevance in the synthesis

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of the complete infinite chain. Here, we are defining an incomplete infinite chain as an inorganic building unit that extends infinitely along a given Cartesian axis but is missing one or more of the canonical ligands (e.g., HO or RCO₂) responsible for interconnectivity between orthogonal dimensions. Note that this approach still allows for self-assembly of either a 2-dimensional MOF or a 1-dimensional coordination polymer.

In order to populate solution with the incomplete building unit, nonpolymerizable monotopic capping ligands are deployed. These ligands compete with the polymerizable ligands, inhibiting polymerization on at least one Cartesian axis while ensuring coordinative saturation of the metal center. This approach permits the inorganic infinite chain to form but prevents full 3-dimensional connectivity of the framework (Figure 1). Our previous work centered on using halide

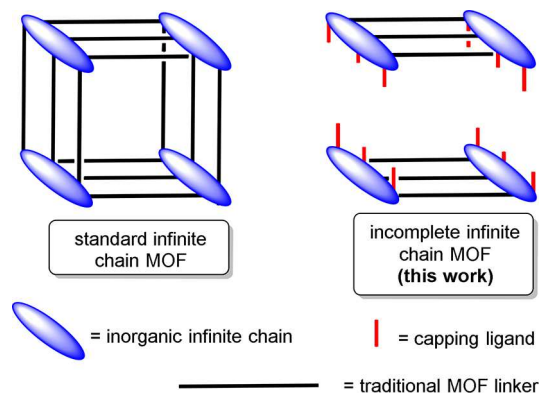


Figure 1. Schematic representation of the formation of MOFs containing an incomplete infinite chain.

capping ligands, which has proven successful when studying MOFs synthesized from metal halide precursors.²¹ While our former strategy relied on manipulating the metal-halide ligand dissociation equilibrium, we posited that a complementary strategy might be necessary for MOFs synthesized from metal nitrates. To this end, we proposed a system in which the polymerizing linker contains the capping ligand, an approach that engenders chelation of the ligand with the growing metal chain. Herein, we report four new MOFs containing “incomplete” infinite chains synthesized from organic components bearing both carboxylate and sulfur-derived moieties.

Treatment of Al(NO₃)₃ with 2,5-dimercaptoterephthalic acid in water at 180 °C yielded a new MOF, YCM-61 (YCM = Youngstown Crystalline Material) (Figure 2). YCM-61 is a two-dimensional (2-D) MOF comprised of square lattice-like sheets, where the functionalized terephthalate linkers are connected through an “incomplete” infinite chain consisting of cationic octahedral aluminum centers with the general formula [Al(CO₂R)(OH)(OH₂)₂]⁺. The *trans* water ligands prevent the sheets from connecting along the layer-stacking axis. Each cationic Al-center is balanced by an anionic sulfonate group, putatively formed *in situ* via oxidation of the linker thiol moieties by endogenously generated nitric acid.²³

Solid-state Raman spectroscopy of YCM-61 revealed a vibration at 782 cm^{−1} (Figure S12). Considering that the PNBu previously observed by Distaso and Hartmann presents a solution-phase vibration at 780 cm^{−1}, we posit that the [Al(CO₂R)(OH)(OH₂)₂]⁺ node found in YCM-61 could be

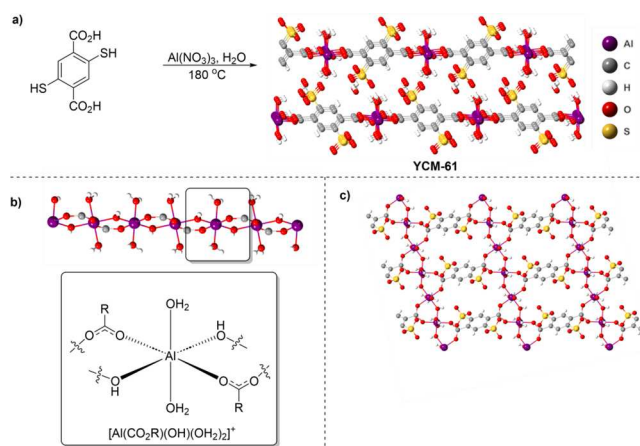


Figure 2. a) Synthesis of YCM-61. b) Representation of the infinite chain with a schematic representation of the coordination sphere around a single Al-center. c) A single layer of YCM-61.

an alternative polymerizing species to the previously proposed [Al(H₂O)₄(CO₂R)]²⁺ molecular structure.^{16–18}

Synthesis of an In-analog of YCM-61 was successful, albeit in a partially dehydrated form. The new MOF, YCM-71, was synthesized from In(NO₃)₃ and 2,5-dimercaptoterephthalic acid in water at 220 °C (Figure 3). Unlike YCM-61, YCM-71

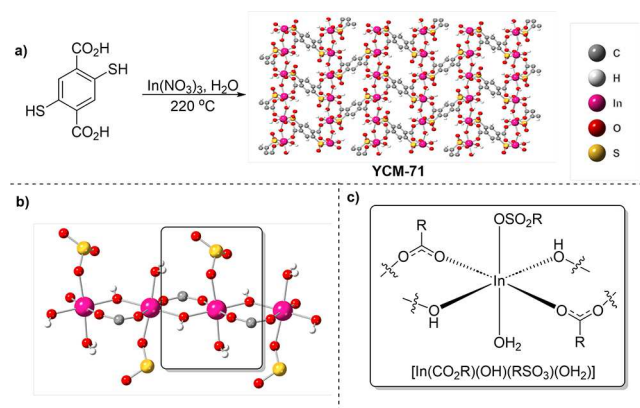


Figure 3. a) Synthesis of YCM-71; note that guest waters have been removed from the pores for clarity. b) Representation of the infinite chain. c) Schematic representation of the coordination sphere around a single In-center.

is connected along all three Cartesian axes and contains a neutral infinite chain with the formula [In(CO₂R)(OH)(RSO₃)(OH₂)]. The difference in connective dimensionality occurs because a sulfonate group—once again formed by *in situ* oxidation of the thiols—is now coordinated to the In-center.

In an attempt to synthesize a molecular analog of YCM-71, In(NO₃)₃ was treated with 2-thiosalicylic acid at 120 °C in water. It was hypothesized that the absence of a second carboxylate on the ligand would prevent polymerization. However, a new 2-dimensional MOF, YCM-72, formed (Figure 4). YCM-72 also contains a neutral infinite chain with the formula [In(CO₂R)(OH)(RSO₃)(OH₂)]. The two-dimensional layers are tightly stacked in the solid state in an ABAB repeating pattern.

A second effort to synthesize a molecular analog of YCM-71 (and YCM-72) using sodium 3-sulfobenzoate as the ligand

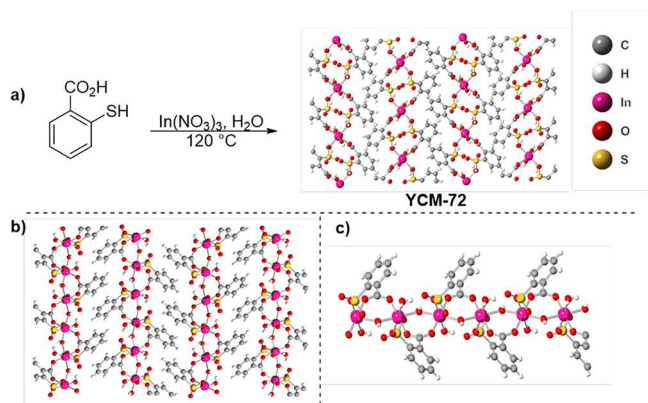


Figure 4. a) Synthesis of YCM-72. b) Multiple layers of YCM-72. c) A single layer of YCM-72.

yielded a second new two-dimensional MOF, YCM-73 (Figure 5), containing a neutral infinite chain with the formula

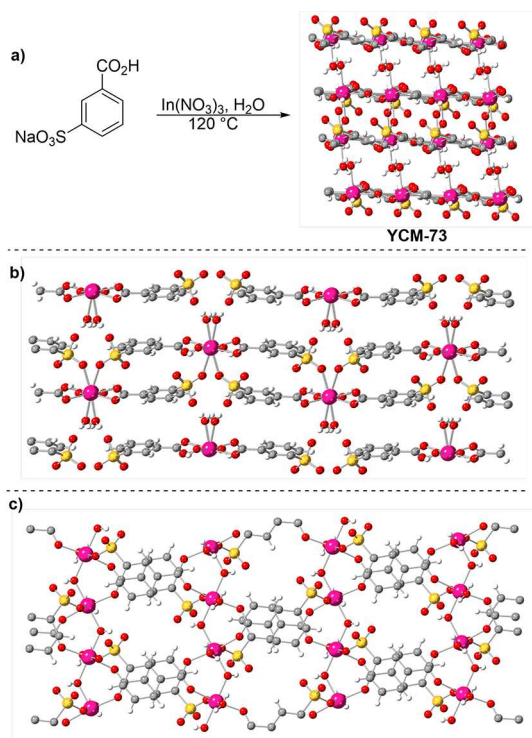


Figure 5. a) Synthesis of YCM-73. b) Layers of YCM-73 stacked. c) A single layer of YCM-73.

$[\text{In}(\text{CO}_2\text{R})(\text{OH})(\text{RSO}_3)(\text{OH}_2)]$. YCM-73's layers are themselves three-dimensionally connected, as the In-chains are in

alternating planes. Attempts to synthesize molecular analogs of YCM-61 using 2-thiosalicylic acid and 3-sulfobenzoate were unsuccessful and did not yield aluminum analogs of YCM-72 or -73.

Solid-state Raman spectroscopy of YCM-71, -72, and -73 revealed vibrations at 776 cm^{-1} , 741 cm^{-1} , and 753 cm^{-1} respectively. We hypothesize that these frequencies are analogous to the Al-species vibration associated with YCM-61 found at 782 cm^{-1} .

YCM-61, -71, -72, and -73 were tested for stability when exposed to water, 1 M $\text{HCl}_{(\text{aq})}$, 1 M $\text{NaOH}_{(\text{aq})}$, acetic acid, acetonitrile, *N,N*-dimethylformamide (DMF), and ethanol for 7 days at room temperature. All samples were analyzed using powder X-ray diffraction (Table 1). All four MOFs were stable in acetic acid, acetonitrile, DMF, and ethanol. YCM-61 proved stable in water and 1 M HCl. While YCM-71 was stable in water, it did not tolerate 1 M HCl or 1 M NaOH. Both YCM-72 and -73 did not withstand exposure to water, 1 M HCl, or 1 M NaOH (Figures S8–S11). The increased stability of the Al-derived YCM-61 compared to the In-derived YCM-7X series is consistent with previous reports on the stability of group 13 MOFs.²⁴

We have reported the synthesis of four “intermediate MOFs” containing incomplete infinite chains. The strategy of deploying intramolecular sulfonate as either a charge-balancing or chelating functional group has proven effective and will be explored in other MOF systems. Whether the inorganic building units found in YCM-61, -71, -72, or -73 represent true mechanistic intermediates in the formation of group 13 infinite chains will continue to be investigated. Lastly, the relevance of these MOFs as analogs for mechanistic intermediates for other $+3 [\text{M}(\text{OH})(\text{O}_2\text{CR})_2]_\infty$ infinite chain-containing MOFs is being investigated, and the results of those studies will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.4c00508>.

Synthetic and spectroscopic experimental details, single crystal X-ray, PXRD, TGA, and Raman data (PDF)

Accession Codes

CCDC 2342369–2342372 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1. Solvent Stability Analysis of YCM-61, -71, -72, and -73

Solvent	YCM-61	YCM-71	YCM-72	YCM-73
Water	Stable	Stable	Phase change	Decomposed
1 M $\text{HCl}_{(\text{aq})}$	Stable	Dissolved	Dissolved	Dissolved
1 M $\text{NaOH}_{(\text{aq})}$	Dissolved	Decomposed	Decomposed	Decomposed
Acetic acid	Stable	Stable	Stable	Stable
Acetonitrile	Stable	Stable	Stable	Stable
DMF	Stable	Stable	Stable	Stable
Ethanol	Stable	Stable	Stable	Stable

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Notes

The authors declare no competing financial interest.

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