Ultrastable High-Connected Chromium Metal-Organic Frameworks

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ABSTRACT: The state-of-the-art MOFs are generally known for chemical stability at one end of the pH scale (i.e., pH < 0 or pH > 14). Herein, we report new Cr-MOFs capable of withstanding extreme pH conditions across approximately 16 pH units from pH < 0 to pH > 14, likely the largest observed pH range for MOFs. The integration of multiple stability-enhancing factors including nonlabile Cr^{3+}, mixed Cr-N and Cr-O crosslinks, and the highest possible connectivity by Cr_3O trimers enables extraordinary chemical stability confirmed by both PXRD and gas adsorption. Notably, the base stability is much higher than literature Cr-MOFs, thereby revitalizing Cr-MOF's viability in the pursuit for the most chemically stable MOFs. Among known cationic MOFs, the chemical stability of these new Cr-MOFs is unmatchable, to our knowledge. These Cr-MOFs can be developed into multi-series of isoreticular MOFs with rich potential for functionalization, pore size and pore geometry engineering, and applications.

Cr^{3+} is known for its potential to form MOFs with remarkable stability due to its kinetic inertness and high charge/radius ratio,[1-7] and yet this potential remains largely unrealized. In fact, despite coming onto the MOF scene early,[8,9] Cr-MOFs have been somewhat overshadowed in recent years by newer stable MOFs.[10-16] This is in part due to the practicality of crystal growth where lability of metal ions plays a big role. Cr-MOFs are hard to crystallize, even though Cr^{3+} can easily fit into many structural patterns based on the consideration of charge and ionic radii. A look at the decade-long synthetic development of Cr- and Zr-MOFs reveals an interesting disparity: Cr-MOFs first appeared as low-connected structures (≤ 6) whereas Zr-MOF made its debut as a high-connected framework (12 in UiO-66).[8,9,17] For achieving high chemical stability, Zr-MOF enjoys an advantage over Cr-MOFs with its high-nuclearity cluster (e.g., Zr_6) and related high connectedness.[18,19] However, Cr-MOF has it own advantages. For example, when designing Cr^{3+} MOFs, we have available a vast amount of knowledge from studies of other metal types (with comparable charge and/or radii) such as Al^{3+} or Fe^{3+},[20,21] mixed Co^{2+}/V^{3+}, and even M^{2+} ions (e.g., $Zn_3(OH)$-based).[22-24] This knowledge includes various topologies useful as synthetic targets for Cr-MOFs.

Currently, Cr-MOFs are well known as 6-connected Cr_3O-trimer-based MOFs such as MIL-88(Cr) and MIL-101(Cr).[19,25,26] Researchers have developed novel strategies to introduce Cr^{3+} into MOFs. For example, one method makes use of labile metal ions such as Zn^{2+} as links to bridge chromium trimers. Unsurprisingly, the incorporation of labile metal ions compromise chemical stability normally expected from Cr-MOFs.[27,28] Another method is to introduce Cr^{3+} via post-synthetic modifications.[29,30] However, the structures amenable to fast-enough metal-node exchange are usually low-connected and are intrinsically less stable compared to high-connected (≥ 9) topologies. After nearly two decades since the first report of Cr-MOF, there are still few Cr-MOFs. Furthermore, known low-connected Cr-MOFs have limited stability, especially in basic solution (pH≤12).[29,31,32]

To make new Cr-MOFs with superior stability, going beyond currently known 6-connected-Cr_3O frameworks is a worthy pursuit. High-connected Cr-MOFs are expected to be difficult to crystallize, given what we know about low-connected Cr-MOFs. Additionally, M_3O/OH trimers have two types of coordination sites (i.e., edge and corner of a triangle) and may be best served with a combination of two types of ligands. This multi-component assembly makes it far less likely to form 9-connected MOFs via chance events compared to MOF topologies for which one type of ligands (e.g., a dicarboxylate) suffices. The aforementioned factors have contributed to the lack of 9-connected Cr-MOFs prior to this work. The 9-connected framework is desirable for pushing the boundaries of chemical stability by Cr-MOFs.

Since 2009, we have reported several new structural models including the cage-in-cage concept (e.g., CPM-5, CPM-24) for pore-space partition of MOFs.[33-35] One of such models has fascinating bi-directional structure-

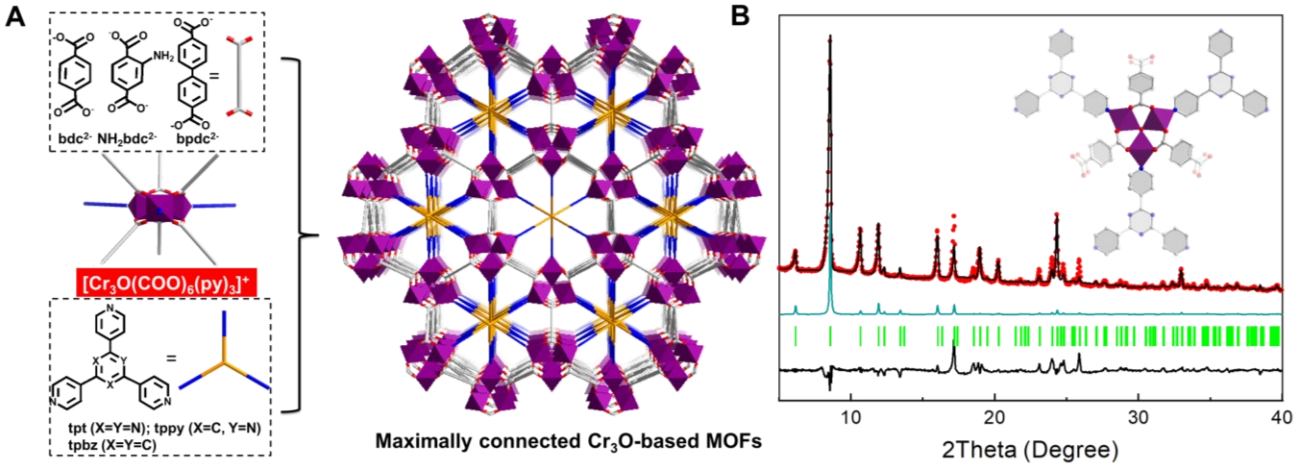

Figure 1.(A) Illustration of the structural components, together with the framework viewed along the *c* axis. (B) Observed (red), Rietveld-refined (blue), and calculated (cyan) PXRD patterns of CPM-243(F) (inset: 9-connected Cr trimer). The difference plot and the Bragg positions are shown in black and green, respectively. NH_2bdc^{2-} = 2-aminoterephthalate, $bpdc^{2-}$ = biphenyl-4,4'-dicarboxylate), tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine, tpbz = 1,3,5-tri(4-pyridyl)-benzene, tppy = 2,4,6-tris(4-pyridyl)pyridine.

directing effects between MIL-88-type framework (made of metal trimers and ditopic ligands) and tritopic pore-partition ligands.[36,37] Of particular inspiration to this work is the observation that the pore-partition ligand such as tpt can readily direct the formation of uncommon metal-trimer compositions (e.g., Co_2V, Mg_2Ti).[24] The synergistic effects from the MIL-88 framework and pore-partition ligands make this structure type (denoted **pacs**) a versatile platform that can be exploited to address multiple challenges facing MOF materials. In this work, we focus on a decades-old challenge: the synthesis of high-connected (> 6) Cr-MOFs that could expand the boundaries of chemical stability for MOFs.

Here we report a family of simultaneously acid- and base-resistant Cr-MOFs. Excluding variants due to the use of different modulators, five Cr-MOFs with the pacs topology and one Cr-MOF with the ncb topology,[38] all of which are 9-connected, have been made. The pacs members were made by changing ditopic linkers or by varying tritopic pore-partition ligands. In addition to Cr-bdc-tpt (denoted **CPM-243**), other structures include CPM-243-tpbz, CPM-243-tppy, CPM-244 (Cr-NH_2bdc-tpt), and CPM-249 (Cr-bpdc-tpt) (Figure 1).

In terms of the toughness against strong acids and strong bases, CPM-243(F) synthesized with HF covers perhaps the widest range in the pH unit (pH ≈ -1 to 15), from 12 M HCl to around 5 M NaOH, when evaluated by both PXRD and gas sorption. The resistance towards strong bases is noteworthy: CPM-243(F) is much more stable than Cr-MOFs reported before. Such a higher stability comes from 9-connected Cr_3O trimer with a mix of Cr-O and Cr-N bonds. CPM-243 is highly tunable and could be expanded into multiple isoreticular series. Furthermore, due to the pore-partition-ligand-assisted elimination of pendant ligands such as F^-/OH^- in otherwise low-connected structures, these 9-connected Cr-MOFs have cationic framework, making them excellent candidates for applications involving mobile anions under harsh chemical conditions.

CPM-243 (Cr-bdc-tpt) was synthesized by hydrothermal reaction of $Cr(NO_3)_3{\cdot}9H_2O$, H_2bdc, tpt with acid modulator at 220 °C. While multiple acid modulators including hydrofluoric acid, formic acid, acetic acid, and benzoic acid could lead to CPM-243, the phase with the best crystallinity currently comes with HF and is denoted CPM-243(F) (Figure S1). The framework of CPM-243 is built via cooperative assembly between pore-partition ligand (tpt) and MIL-88/MOF-235-type (the **acs** net) framework,[17,39] resulting in the partitioned acs net, known as **pacs** net. CPM-243 was prepared in the polycrystalline form and was identified by comparing its powder diffraction pattern with that simulated from single-crystal data of CPM-33a made from Ni.[37] The Rietveld refinement gave a good fit between the refined pattern and the experimental one with low residual value (Figure 1 & Table S1).

A key feature achieved in this work for Cr-MOFs is three extra intercluster crosslinks offered by tripyridyl ligands via Cr-N bond. Cr-trimer MOFs known so far have pendent ligands (e.g., F^-/OH^-/H_2O/pyridine) and correspondingly low-connected frameworks.[40] In CPM-243, the N-donor tpt is attached to three separate Cr-trimers and in the meantime excludes terminal coordination species like F^-. We suggest a thermodynamic driving force called the multi-point binding mechanism in which one neutral polytopic ligand such as tpt (Scheme S1) simultaneously makes three bonds to the framework and displace three terminal ligands. This is an entropy-driven process, akin to the chelate effect.

The integration between pore-partition ligands and nonlabile Cr^{3+} is ideally suited for generating MOFs with chemical stability in the widest possible pH range. Overall, the presence of the multi-binding pore-partition ligand, high-connectivity and framework rigidity, and inert Cr-O/Cr-N bonds greatly increases the difficulty of a nucleo-

philic substitution, making these new Cr-MOFs highly resistant to chemical attack by coordination species such as OH^- and boiling water. The exceptional acid stability of new Cr-MOFs is largely due to the high charge/radius ratio of Cr^{3+} and ligand field stabilization energy maximized by its d^3 configuration (for the weak-field ligands such as dicarboxylates).

The gas adsorption properties were investigated (Figure S3-11). N_2 adsorption at 77 K shows that the surface areas of CPM-243 can be tuned by the type and the amount of acid modulators which impact crystallinity.[41] The synthesis conditions optimized for sorption properties remain undetermined, given the large number of possible permutations in synthetic parameters. Pristine CPM-243(F) synthesized under the conditions reported here has the BET and Langmuir surface areas of 1123.0 and 1213.6 m^2/g, respectively. It can adsorb 130 cm^3/g of CO_2 at 273 K and 1 atm (Table S2), a good value among base-stable MOFs (e.g., 29.3 cm^3/g of CO2 by ZIF-8).[42]

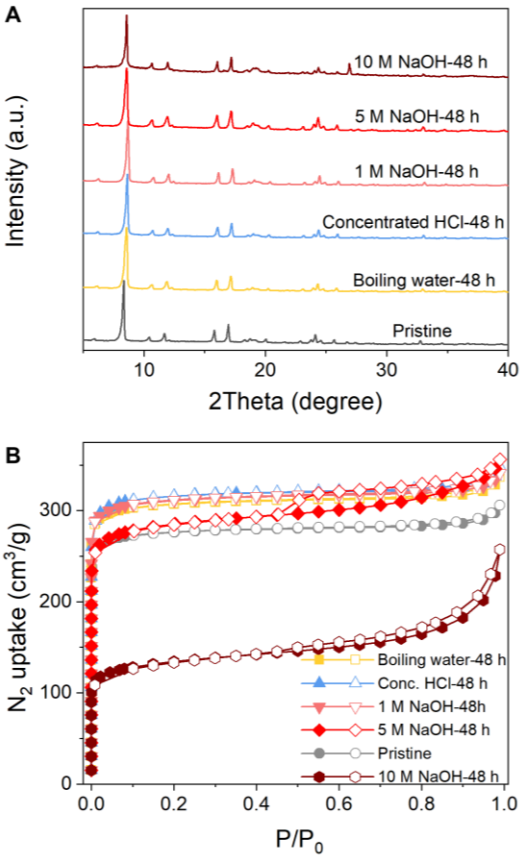

Figure 2. (A) PXRD patterns and (B) N_2 adsorption isotherms at 77 K of pristine and treated CPM-243(F).

CPM-243(F) has the highest thermal stability among Cr-trimer based MOFs. From TGA, the steep weight loss started at 500 °C (Figure S12). PXRD shows that CPM-243(F) is stable to about 400 °C (Figure S13). In comparison, low-connected MIL-101 (Cr) and MIL-100 (Cr) were reported to be stable up to 275 °C.[19,26] The stability of MIL-88(Cr) is unclear by PXRD and/or gas sorption, and is below 350 °C from TGA.[43]

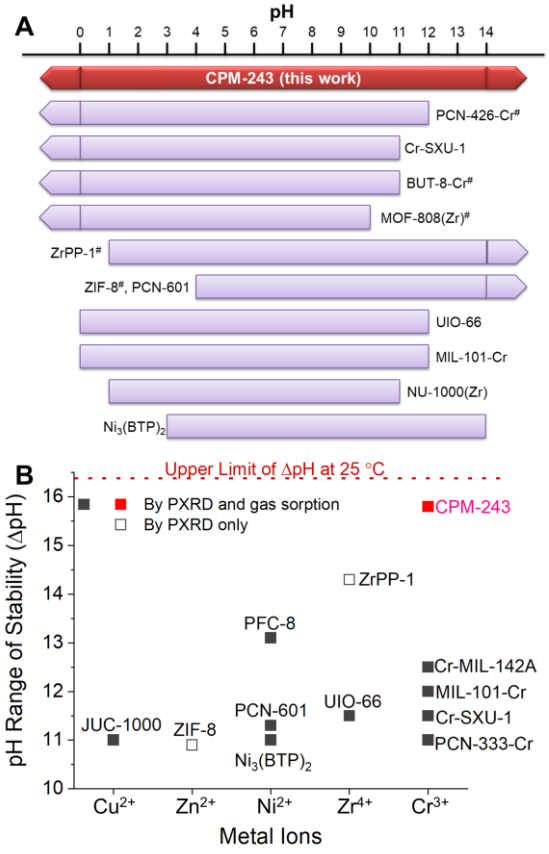

Figure 3. (A) Stability comparison of select stable MOFs. The arrow indicates stability under pH<0 or pH>14. # means stability according to PXRD. (B) The stability range defined by the difference between low and high pH values for select MOFs. The red-dotted line represents the limit of pH range (16.4) from concentrated HCl (12 M, pH=-1.1) to saturated NaOH (19 M, pH=15.3).

The chemical stability of CPM-243(F) was tested in boiling water and different acid-base solutions from concentrated HCl (12 M) to saturated NaOH (19 M). PXRD indicated that CPM-243(F) retained high crystallinity under boiling water and harsh solutions from concentrated HCl to 5 M NaOH solution (Figure 2A & Figure S14). Encouragingly, gas sorption properties actually improve following these treatments, likely due to additional sample activation effect. (Figure 2B).[44,45] N_2 adsorption further confirmed the robustness of CPM-243 from concentrated HCl to 5 M NaOH. But it is notable that a decrease in N_2 uptake was observed after treatment in 10 M NaOH (Figure S15). In addition to PXRD and N_2 adsorption, we also kept track of the change in the sample mass following different treatments. The normalized results showed negligible sample loss during treatments from concentrated HCl to 5 M NaOH, further supporting the ultrahigh stability of CPM-243 (Table S3).

In Figure 3B, we use the difference in pH values (ΔpH = pH_{base}- pH_{acid}) to compare the chemical stability of select stable MOFs, which highlights the exceptional stability of CPM-243(F) among stable MOFs.[31,46-52] The resistance to strong bases by CPM-243 is notable, considering that no prior Cr-MOFs have the basic resistance higher than pH of 12. The basic resistance of CPM-243 is much higher than known carboxylate MOFs. The acidic resistance of CPM-243 is also among the highest. There are few MOFs capable of withstanding concentrated acidic solution like 12 M HCl, although a certain leve of resistance to acidic solutions is common for MOFs made of high-valent (≥ 3) metals and carboxylate ligands, (Figure 3 & Table S4).

In summary, a family of new Cr-MOFs based on 9-connected Cr trimers is reported. With the integration of Cr^{3+}, the introduction of N-donor ligands, and high-connected metal trimers, CPM-243 shows exceptional chemical robustness. In particular, CPM-243 could be stable in the perhaps widest range of pH values from pH < 0 to pH > 14. These materials can enable the study of various MOF properties in a broad range of chemical systems without limitations imposed by pH or solvent environment. Quite uniquely among stable MOFs, this work shows the feasibility to achieve exceptional chemical stability even among cationic MOFs, among which few chemically stable forms are known.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge on the ACS Publications website.
Experimental Procedures and compound characterization data (PDF)
Crystallographic data with CCDC Nos. 2102217, 2102362 (CIF)

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Notes

The authors declare no competing financial interests.

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