

Synthesis of Novel Amino Acid-Based Metal Organic Framework

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Hypothesis

An amino acid can be attached to cyanuric chloride to make an organic linker, which can be used as a reactant with a metal to form a novel amino acid-based metal organic framework.

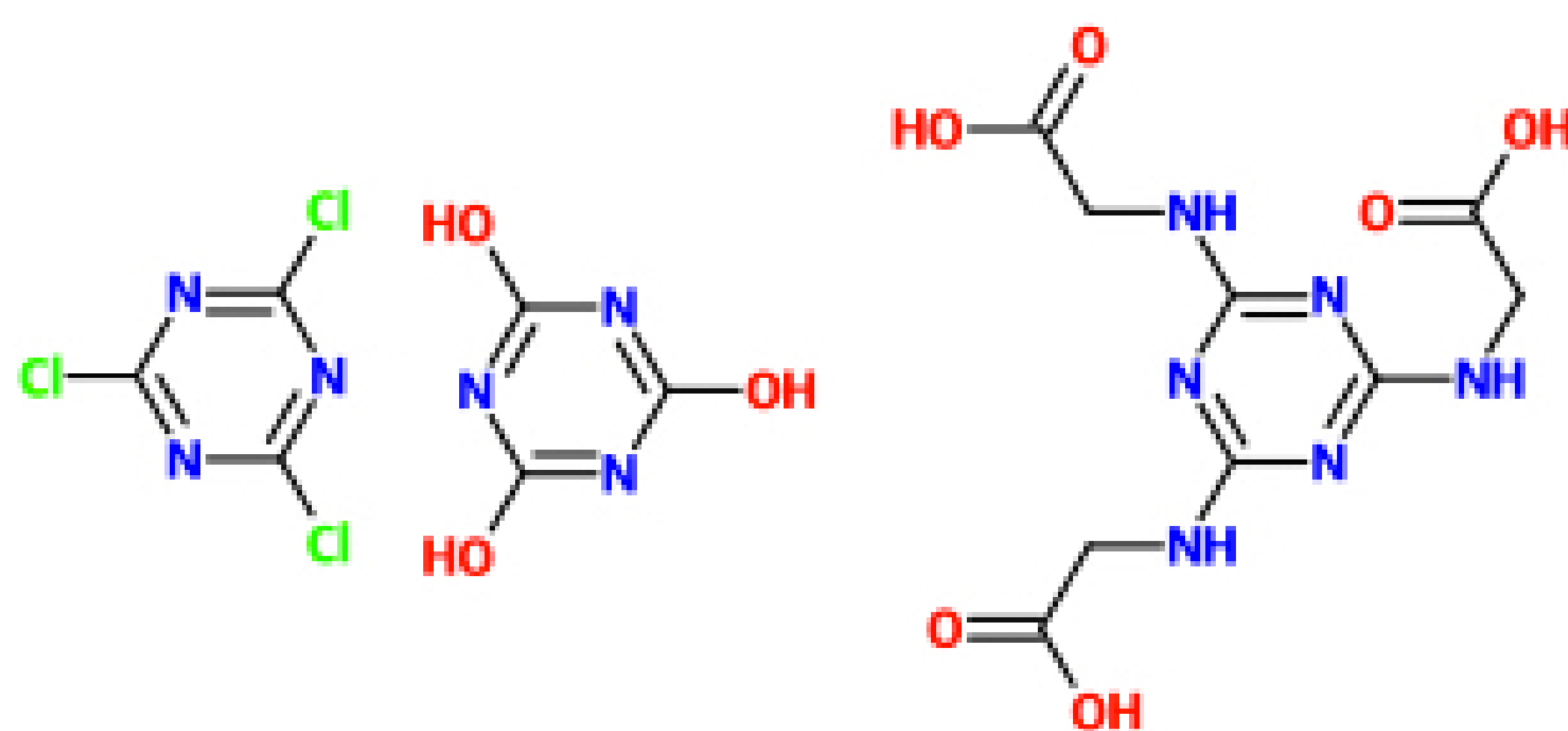


Figure 1. To the left shows the reactant, cyanuric chloride. In the middle is cyanuric acid, the byproduct compound. To the right shows the compound we have successfully synthesized, as verified by NMR analysis (H and C¹³).

Results

The amino acid-based linker was successfully synthesized using inexpensive materials, and the structure was characterized by NMR (H and C¹³). A copper-based MOF has been synthesized with this linker through solvothermal techniques. The synthesized material show signs of a porosity with surface areas of ~ 50 m²/g. Through various observations, oxidation during the activation process is believed to have occurred since the MOF turned brown after the activation when the initial color was blue/green. During the first few synthesis runs for the alanine linker, no product formed. It was determined through NMR analysis (H and C¹³) that hydration of cyanuric chloride occurred as a side reaction, which formed cyanuric acid as the byproduct.

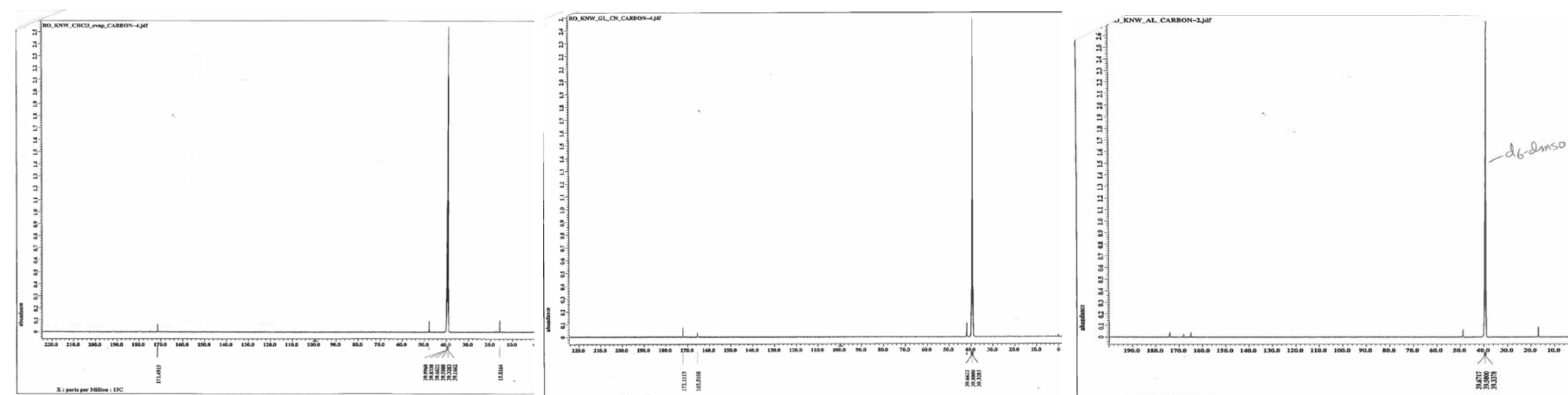


Figure 2. To the left is the NMR of the hydrated cyanuric chloride (cyanuric acid). This NMR let us know that we were running our experiment too long and too hot. In the middle is NMR of the glycine linker. We predicted three peaks representing three carbons each, which is consistent with our data. To the right is the NMR of the disubstituted alanine linker. This is the NMR of the solid that formed after attempting to synthesize the alanine linker. Through the NMR, it is revealed that we successfully attached two alanine molecules onto the cyanuric chloride.

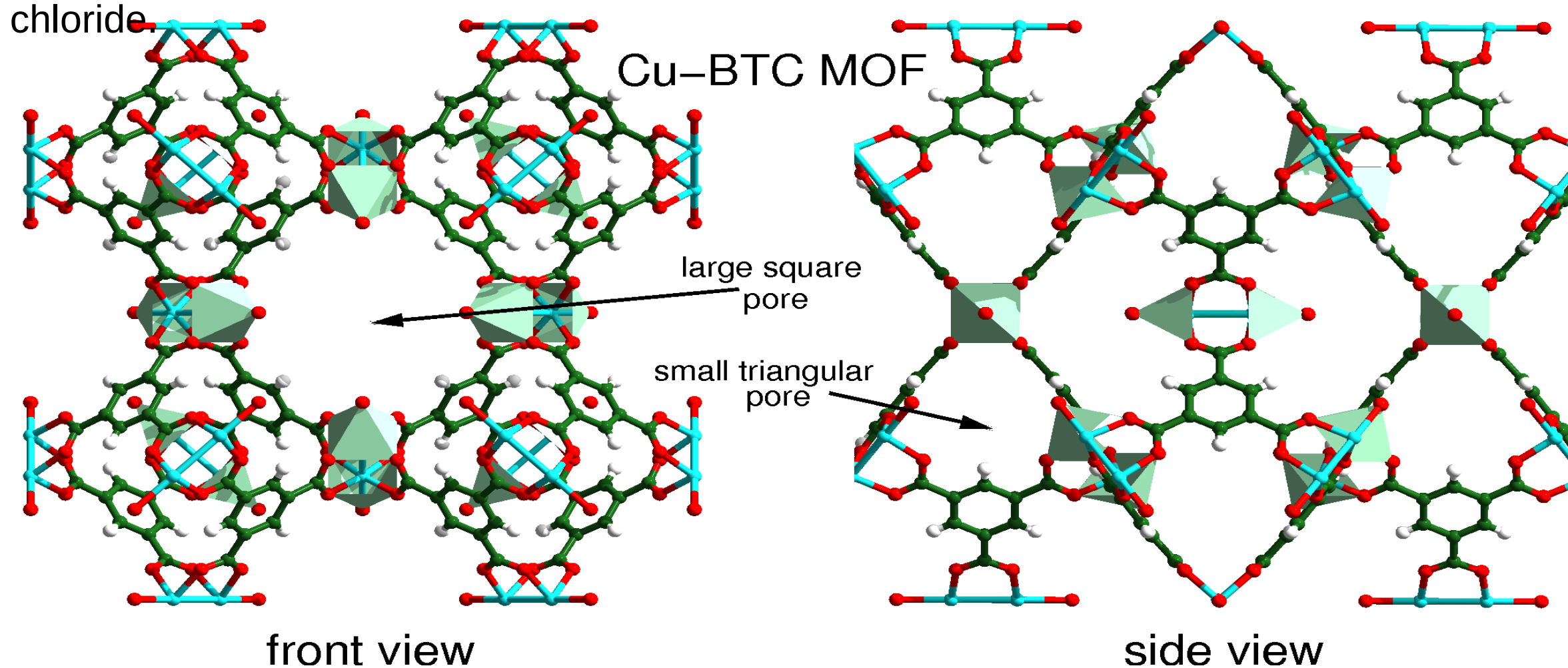


Figure 3. Above: two views of a Cu₃(BTC)₂(H₂O)₃ Metal-Organic Framework (MOF) system. With approximate DFT methods, systems of this size can be routinely modeled. Retrieved 2015 from the SCM (Scientific Computing & Modeling), <https://www.scm.com/News/QUASINANO.html>

Abstract

Porous materials are an important component in many adsorbents and catalysts in the chemical industry. Recently, a new class of materials, metal-organic frameworks, or MOFs, have shown promise as high surface area materials with interesting chemical properties. MOFs are comprised of metal cations connected by organic linker molecules; it is the geometry between metal and the linker which creates the structure and the porosity. In this work, a linker molecule was synthesized using an amino acid and cyanuric chloride to create a novel nanoporous compound. Although a porous structure was formed, experiments to maximize its porosity are still needed to accurately characterize the compound as a MOF. Once the synthesis conditions have been optimized, the adsorption capability of the new material will be characterized. Based on its chemical structure, we anticipate that CO₂ adsorption will be exceptionally high, which has applications for CO₂ capture in energy production and recirculated air for spacecraft and submarines.

Methods

Synthesis of Amino Acid-Based Linkers

To synthesize our amino acid-based linkers, sodium bicarbonate, glycine, and water were combined in a beaker and stirred. In a round bottom flask, cyanuric chloride and chloroform were combined and stirred. After each material dissolved, the aqueous solution was combined into the flask. The flask was placed on a heating mantle with a condenser attached on top. The heating mantle was set to 45° C. The solution was stirred and heating for a week. After a week, the solution was cooled to room temperature and the organic layer was removed. Hydrochloric acid was added into the aqueous solution until the pH reached 2 and precipitate finished forming. The product was filtered and stored.

Synthesis and Activation of Amino Acid-Based Copper MOFs

The amino acid-based MOFs were synthesized according to the literature⁸. Glycine linker was mixed into a 1:1:1 solution of DMF/EtOH/Water. Copper (II) nitrate trihydrate was mixed with the same solution of equal volume. Once each solid dissolved, they were combined and stirred for 23 hours. After 23 hours, triethylamine was added. The product was filtered and stored in a round bottom flask with heat and vacuum pulled.

Surface Area Measurement

Once the MOF was activated, it was placed into a glove bag containing N₂. While in the glove bag, the MOF was transferred into a test tube. The mass of the MOF was recorded. The test tube was attached to the Nova 4200e. The Nova pulled vacuum, and then inserted nitrogen gas in increments and measured the amount adsorbed onto the MOF. After the Nova finished analyzing, a linear fit for the multi-point BET was found and the surface area was recorded.

Conclusions

•Glycine and cyanuric chloride can be combined to successfully synthesize and organic linker.

•A nanoporous material can be successfully synthesized from the amino acid based linker, but the structure still needs to be optimized to be classified as a MOF.

Future Directions

•Additional synthesis procedures will be tested to optimize the surface area of the glycine-linker MOF.

• Further experiments are being tested to determine an optimal way to synthesize the alanine linker.

• Analysis of each MOF before and after activation using x-ray diffraction to verify the structure of the crystallized material to determine which MOF synthesis conditions are appropriate.

Literature Cited

- (1) Lee, Y.-R.; Kim, J.; Ahn, W.-S. Synthesis of Metal-Organic Frameworks: A Mini Review. *Korean J. Chem. Eng.* **2013**, *30* (9), 1667–1680.
- (2) Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2012**, *112* (2), 933–969.
- (3) Khoshhal, S.; Ghoreyshi, A. A.; Jahanshahi, M.; Mohammadi, M. Study of the Temperature and Solvent Content Effects on the Structure of Cu–BTC Metal Organic Framework for Hydrogen Storage. *RSC Adv* **2015**, *5* (31), 24758–24768.
- (4) Zhang, B.; Zhang, J.; Liu, C.; Sang, X.; Peng, L.; Ma, X.; Wu, T.; Han, B.; Yang, G. Solvent Determines the Formation and Properties of Metal–organic Frameworks. *RSC Adv* **2015**, *5* (47), 37691–37696.
- (5) Parshamoni, S.; Sanda, S.; Jena, H. S.; Konar, S. A Copper Based Pillared-Bilayer Metal Organic Framework: Its Synthesis, Sorption Properties and Catalytic Performance. *Dalton Trans.* **2014**, *43* (19), 7191.
- (6) Calleja, G.; Sanz, R.; Orcajo, G.; Briones, D.; Leo, P.; Martínez, F. Copper-Based MOF-74 Material as Effective Acid Catalyst in Friedel–Crafts Acylation of Anisole. *Catal. Today* **2014**, *227*, 130–137.
- (7) Schlichte, K.; Kratzke, T.; Kaskel, S. Improved Synthesis, Thermal Stability and Catalytic Properties of the Metal-Organic Framework Compound Cu₃(BTC)₂. *Microporous Mesoporous Mater* **2004**, *73* (1-2), 81–88.
- (8) Nasihat Sheno, N.; Morsali, A.; Woo Joo, S. Synthesis CuO Nanoparticles from a copper(II) Metal-Organic Framework Precursor. *Mater. Lett.* **2014**, *117*, 31–33.
- (9) Adhikari, A. K.; Lin, K.-S. Synthesis, Fine Structural Characterization, and CO₂ Adsorption Capacity of Metal Organic Frameworks-74. *J. Nanosci. Nanotechnol.* **2014**, *14* (4), 2709–2717.

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