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Laboratory Experiment

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Preparation and Analysis of Cyclodextrin-Based Metal−Organic Frameworks: Laboratory Experiments Adaptable for High School through Advanced Undergraduate Students

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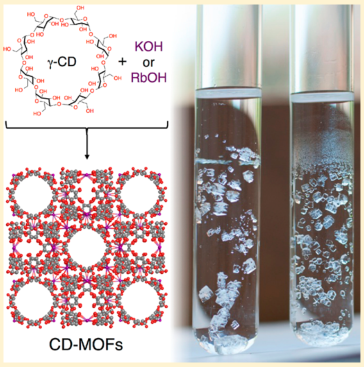
Supporting Information

ABSTRACT: γ-Cyclodextrin can assemble in the presence of KOH or RbOH into metal−organic frameworks (CD−MOFs) with applications in gas adsorption and environmental remediation. Crystalline CD−MOFs are grown by vapor diffusion and their reversible adsorption of CO_2(g) is analyzed both qualitatively and quantitatively. The experiment can be tailored to high school through advanced undergraduate laboratories and engages students in several areas of fundamental chemistry (crystallization, chemical equilibria, acid−base reactions, gas laws), advanced materials (MOFs), and broader impacts of chemistry (renewable resources and environmental chemistry).



KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Laboratory Instruction, Inorganic Chemistry, High School/Introductory Chemistry, Hands-On Learning/Manipulatives, Materials Science, Crystals/Crystallography, Green Chemistry*

Highly porous materials,[1] such as zeolites[2] and activated carbon,[3] have played prominent roles throughout the chemical, materials, and petroleum industries for over a century. Interest in porous materials stems from their varied applications, including catalysis, chemical separations and purifications, and the selective uptake of small molecules. Recently, metal−organic frameworks[4] (MOFs) have generated significant attention for their synthetic tunability and exceptionally high porosity. These crystalline framework solids are composed of metals ions or clusters coordinated to rigid, polyfunctional organic ligands. In many cases MOFs are stable to the evacuation of solvents, leaving behind permanently porous molecular scaffolds with surface areas that commonly exceed 1000 m^2/g. One especially attractive aspect of synthetic MOFs is the modularity of their design as afforded by the multitude of available metal "nodes" and polyfunctional organic "linkers." This modularity provides significant control over the size, shape, and functionality of the pores within MOFs, which aids in tailoring their structure to specific functions.

While interest in MOFs has increased substantially in both industrial and academic settings, there are currently few experimental protocols[5−7] suitable for introducing MOFs to undergraduates in a laboratory setting and no reports of MOF experiments suitable for advanced high school students have appeared in this *Journal*. This can likely be attributed to the fact that the synthesis of MOFs commonly requires hazardous solvents, high reaction temperatures, and/or expensive starting materials. Similarly, high school and undergraduate laboratories often lack student access to the instrumentation commonly used to characterize MOFs, e.g., powder X-ray diffraction, single-crystal X-ray crystallography, and gas sorption equipment.

The laboratory experiment described herein details the facile synthesis[8] of crystalline MOFs from benign starting materials along with straightforward methods for observing and measuring their uptake of CO_2(g). A particularly appealing aspect of the laboratory experiment is its use of γ-cyclodextrin (Figure 1A−C), a renewable raw material that is a natural degradation product of corn and potato starch, as the polyfunctional organic linker. The environmental implications[9] of using a renewable resource (γ-cyclodextrin) to prepare advanced framework materials (MOFs) capable of capturing a common greenhouse gas (CO_2) will be of particular interest to students. Furthermore, three different formats are described for the preparation and analysis of cyclodextrin-based MOFs (CD−MOFs, Figure 1D,E), allowing the experiment to be tailored to the laboratory skills of different students and the institutional resources of various high schools and colleges/universities. Recommendations for which procedures are most appropriate for each audience, as well as differences in expected results, are provided in the Supporting Information. Through their experience performing this laboratory students gained an

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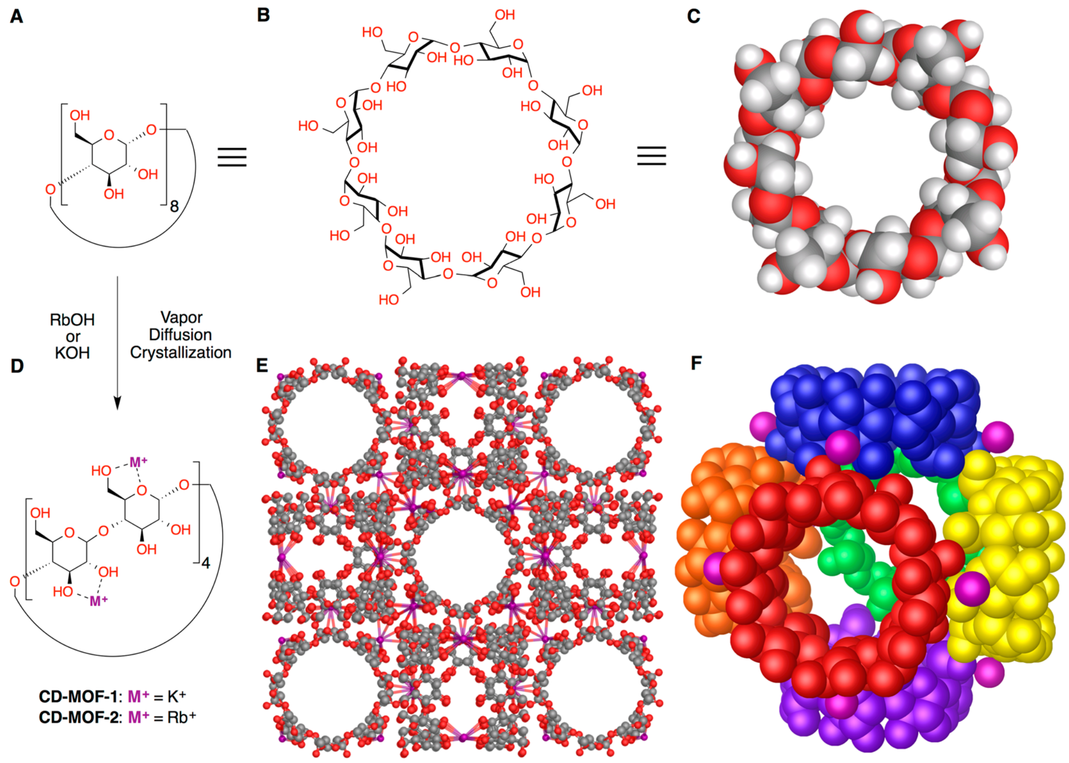

Figure 1. Three different representations of the chemical structure of γ-cyclodextrin: (A) condensed, (B) expanded, and (C) space-filling. (D) Crystallization of γ-cyclodextrin in the presence of RbOH or KOH results in coordination between the metal cations and γ-cyclodextrin, giving rise to porous metal−organic frameworks (CD−MOFs) as shown in (E) and (F). Metal cations are colored purple in (D−F). Individual γ-cyclodextrin macrocycles are colored in (F) to aid in visualizing their relative locations.

increased understanding of several fundamental and contemporary concepts in chemistry, including crystal growth and crystal structures, coordination chemistry, ideal gas laws, chemisorption and physisorption, porous materials and MOFs, and environmental chemistry.

EXPERIMENTAL OVERVIEW

The preparation and investigation of CD−MOFs can be divided into three sections: (i) crystal growth, (ii) crystal activation, and (iii) analysis. Each of these three sections can be modified and tailored to particular laboratory environments and available instrumentation. The laboratory experiment can be carried out in one extended laboratory period (4−5 h); however, the results are both more reproducible and more pronounced when carried out over two lab periods.

The first section of the experiment involves the preparation and growth of CD−MOF crystals from an aqueous solution of γ-cyclodextrin (0.05 M) and 8 mol equiv of KOH or RbOH. Crystals grown in the presence of KOH lead to CD−MOF-1, while those grown in the presence of RbOH give CD−MOF-2.[8a] Growth of CD−MOF crystals is achieved by vapor diffusion with the conditions for crystal growth (solvent, time, temperature) determined by the time available to carry out the lab. Small CD−MOF-1 crystals suitable for further analysis can be grown within 1−1.5 h by vapor diffusion of acetone into a KOH solution of γ-cyclodextrin at 40 °C. Larger and more robust crystals of CD−MOF-2 can be grown within 72−96 h by vapor diffusion of methanol into a RbOH solution of γ-cyclodextrin at room temperature. Many undergraduate laboratory experiments introduce students to crystal growth by either sublimation or cooling of saturated solutions. The use of vapor diffusion provides students an opportunity to learn some of the many factors that influence crystal size and quality, such as the relative solubilities of reagents and products, solvent vapor pressures and miscibilities, and crystal growth rates. Students may also prepare a control sample by simply grinding γ-cyclodextrin and an appropriate alkali hydroxide (1:8 molar ratio) using a mortar and pestle. The resulting powder will have the same composition as their respective CD−MOFs; however, they will not exhibit the same porous crystalline framework.

The second section of the experiment requires students to activate their newly grown CD−MOF crystals, a process necessary to remove residual water and/or starting materials from the pores within the crystals. Activation is achieved by removal of the solution phase surrounding the CD−MOF crystals and reimmersion of the crystals in either dichloromethane (preferred, though more hazardous) or diethyl ether (less preferred, though less hazardous). This process is repeated three times to ensure effective activation. Students complete the activation of their CD−MOF crystals by either placing them under high vacuum or in an oven at 120 °C for 30 min (or longer, if possible). Students also have the option of activating their CD−MOF crystals in a dichloromethane solution containing methyl red indicator (0.10 M). Under this activation procedure, methyl red will be incorporated into the pores of CD−MOF crystals[8b] and provide a means of visually analyzing their uptake of $CO_2(g)$ via colorimetric acid/base chemistry.

The third section of this experiment involves analysis of the CD−MOFs. Students are asked to quantify the amount of $CO_2(g)$ that can be absorbed within the pores of their CD−MOF crystals. This is achieved by placing the crystals in a $CO_2(g)$-rich atmosphere, which can be easily achieved by placing a vial containing a known amount of CD−MOF inside

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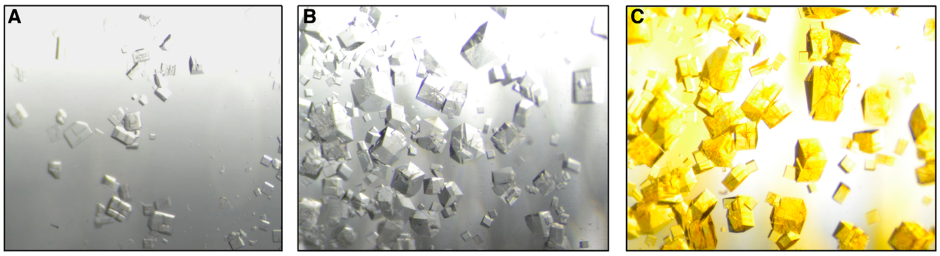

Figure 2. (A) Student-obtained images of KOH-based CD−MOF-1 crystals after 1 h of growth, (B) RbOH-based CD−MOF-2 crystals after 3 days of growth, and (C) RbOH-based CD−MOF-2 crystals after activation with methyl red indicator.

a larger vial containing a few small pieces of solid CO_2. Upon sublimation of some of the CO_2(s) (approximately 5−10 min), students quickly remove their CD−MOF-containing vials and record the mass increase resulting from CO_2(g) adsorption. Quantitative calculation of the CO_2(g) uptake within CD−MOF samples requires that students consider several factors, including: the mass of the crystal sample, the crystal density, CD−MOF adsorption isotherms, and the ideal gas law. Worksheets detailing the calculation of CO_2(g) uptake are provided in the Supporting Information. For samples that have been activated in the presence of methyl red indicator, the adsorption of CO_2(g) can be observed visually: the color of CD−MOF crystals containing methyl red changes from yellow in the absence of CO_2(g) to red upon exposure to CO_2(g). The adsorption and desorption of CO_2(g), and accompanying color change, is reversible and can be repeated several times, providing opportunities for students to observe and discuss concepts of equilibrium, Le Chatelier's principle, and chemisorption and physisorption processes.

■ HAZARDS

An especially appealing aspect of this experiment is its safety and simplicity. The bulk of sample preparations involve aqueous solutions of generally nonhazardous materials. Flammable or otherwise hazardous solvents are used only in small quantities (<10 mL). The solid crystalline CD−MOF products are stable and nonhazardous.[8a]

Personal protective equipment (e.g., gloves, safety goggles, and lab coats) should be worn during all chemical manipulations. γ-Cyclodextrin and methyl red are nonhazardous according to the Global Harmonized System (GHS) of classification and labeling of chemicals; however, general precautions should still be taken to avoid ingestion, inhalation, and contact with the eyes and skin. Alkali hydroxides KOH and RbOH can be irritating to the eyes, skin, and mucous membranes. Methanol, acetone, diethyl ether, and dichloromethane are flammable solvents and should be handled in a fume hood. Methanol is irritating to the eyes, may cause moderate skin irritation, and may be fatal or cause blindness if swallowed. Acetone can be irritating to the skin and should not be inhaled or ingested. Diethyl ether is capable of forming peroxides and must be kept away from any ignition sources. Dichloromethane is a flammable, carcinogenic solvent. Solid CO_2 should be handled using forceps to avoid skin damage by frostbite. All glass vials should be inspected for cracks prior to exposure to high vacuum to avoid risk of implosion. Heat-resistant gloves or forceps should be used when transferring vials into or out of ovens. MSDS sheets for all chemicals should be available to students, and instructors should encourage students to read them prior to starting the experiment.

■ RESULTS

Shown in Figure 2 are pictures of student-obtained CD−MOF crystals grown quickly (Figure 2A), slowly (Figure 2B), and activated with methyl red indicator (Figure 2C). This experiment was carried out at Wesleyan University with students ranging from second-year through advanced, as well as with a group of students from Middletown High School in Middletown, CT. In all cases, students grew single crystals of CD−MOFs using both "fast growth" (1−1.5 h) and "slow growth" (2−7 days) procedures.

Following activation, the most quantitative method of analysis involved measuring the uptake of CO_2(g) upon sublimation of dry ice into vials containing CD−MOF samples. While gas adsorption within the pores of most MOFs is driven by physisorption, CD−MOF crystals adsorb CO_2(g) by a combination of both physisorption *and* chemisorption.[8b,10] At standard temperature and pressure, crystals of CD−MOF-1 and CD−MOF-2 adsorbed 58.3 and 57.5 cm^3 of CO_2(g), respectively, per gram of material. Students must take into consideration not only CO_2(g) adsorption by CD−MOF crystals, but also the increase in mass that arises from displacement of air within the headspace above their specific CD−MOF sample by more massive CO_2(g). Worksheets detailing these calculations are provided in the Supporting Information. Students following this lab procedure grew and activated CD−MOF crystals in 1-dram vials that yielded, on average, 50 mg samples of activated, crystalline CD−MOFs. Upon exposure of these samples to a CO_2(g)-rich atmosphere, the mass increased by an average of 7.2 mg as compared to an ideal increase of 7.5 mg. Mechanically ground control samples averaged a mass increase of 3.4 mg, less than half that of crystalline CD−MOF samples, and their mass uptake can be attributed almost entirely to displacement of air by CO_2(g) within the vial headspace.

Shown in Figure 3 is the reversible adsorption and desorption of CO_2(g) by CD−MOFs along with student-obtained examples of the reversible color change of methyl red-activated CD−MOF-1 upon exposure to CO_2(g). In the absence of CO_2(g), the CD−MOF crystals are yellow, indicating deprotonation of methyl red upon its incorporation and (partial) anion metathesis with hydroxide counterions in the frameworks. Exposure of these yellow CD−MOF crystals to dry ice induced a color change from yellow (pH > 6.2) to red (pH < 4.4) as the CO_2(g) is known to chemisorb into the framework by reacting with a hydroxyl group of γ-cyclodextrin.[8b] This chemisorption process, which partially accounts for the high adsorption of CO_2(g) by CD−MOFs, results in the formation of a carbonate ester and liberation of a proton, which then protonates the methyl red indicator. Removal of the CD−MOF sample from a CO_2(g)-rich atmosphere results in

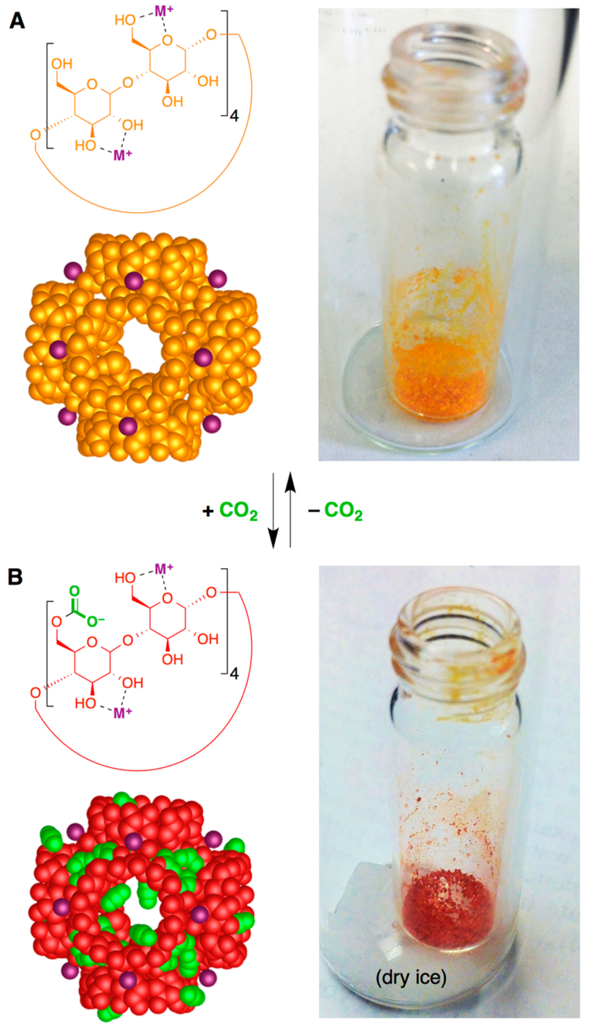

Figure 3. Reversible adsorption and desorption of CO_2(g) by CD−MOFs incorporating methyl red indicator induces a color change from (A) yellow to (B) red. This process is represented structurally, with schematic space-filling models, and with pictures of student-obtained results. Metal cations are represented in purple, and CO_2 and carbonate esters are represented in green. The framework itself does not change color as shown; rather, the color change results from protonation and deprotonation of the methyl red indicator (not shown). Chemical structures and space-filling models are only colored to correlate with the pictured results.

reversion back to its yellow color. Students repeated this process several times to witness the reversibility of this acid−base reaction caused by CO_2(g) adsorption and desorption.

■ SUMMARY

The synthesis and analysis of CD−MOF crystals was found to be of significant pedagogical value to both high school and college students. Students gained experience growing crystals by vapor diffusion and learned about the structures and unique properties of MOFs. Furthermore, the reversible adsorption of CO_2(g) within CD−MOFs required students to think critically about equilibrium, the ideal gas law, chemisorption and physorption processes, and acid−base chemistry. College students who performed this experiment wrote comprehensive lab reports that included a thorough introduction to MOF chemistry along with details of their experimental procedures, results, and interpretation of their results. High school students were given a handout with specific questions designed to help them think more critically about the properties and uses of their CD−MOF crystals. Lastly, and very importantly, this laboratory experiment directly engaged students in topics of renewable resources and environmental remediation. Chemistry has played and will continue to play a central role in these areas, and the sooner students are engaged in discussions of the impacts chemistry can have on the environment (both positive and negative), the better.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Instructors notes, including three recommended experimental procedures that can be adapted to different laboratory settings, student handouts containing detailed instructions for the preparation and analysis of CD−MOFs, and coordinate files for CD−MOF-2 in .pdb, .mol2. and .xyz formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For a recent overview of porous materials and their applications see: Davis, M. E. Ordered Porous Materials for Emerging Applications. *Nature* **2002**, *417* (6891), 813−821.

(2) (a) Cheetham, A. K.; Férey, G.; Loiseau, T. Open Framework Inorganic Materials. *Angew. Chem., Int. Ed.* **1999**, *38* (22), 3268−3292. (b) Tao, Y.; Kanoh, H.; Abrams, L.; Kaneko, K. Mesopore-Modified Zeolites: Preparation, Characterization, and Applications. *Chem. Rev.* **2006**, *106* (3), 896−910.

(3) (a) Boehm, H. P. Some Aspects of the Surface Chemistry of Carbon Blacks and other Carbons. *Carbon* **1994**, *32* (5), 759−769. (b) Moreno-Castilla, C.; Rivera-Utrilla, J. Carbon Materials as Adsorbants for the Removal of Pollutants from the Aqueous Phase. *MRS Bull.* **2001**, *26* (11), 890−894.

(4) For a recent review of metal−organic frameworks (MOFs), see: (a) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341* (6149), 974−986.

(5) Sumida, K.; Arnold, J. Preparation, Characterization, and Postsynthetic Modification of Metal-Organic Frameworks: Synthetic Experiments for an Undergraduate Laboratory Course in Inorganic Chemistry. *J. Chem. Educ.* **2011**, *88* (1), 92−94.

(6) Rood, J. A.; Henderson, K. W. Synthesis and Small Molecule Exchange Studies of a Magnesium Bisformate Metal-Organic Framework: An Experiment in Host-Guest Chemistry for the Undergraduate Laboratory. *J. Chem. Educ.* **2013**, *90* (3), 379−382.

(7) Janssens, N.; Wee, L. H.; Martens, J. A. Esterification Reaction Utilizing Sense of Smell and Eyesight for Conversion and Catalyst Recovery Monitoring. *J. Chem. Educ.* **2014**, *91* (6), 876−879.

(8) This laboratory experiment is inspired by and adapted from: (a) Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.;

Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. Metal-Organic Frameworks from Edible Natural Products. *Angew. Chem., Int. Ed.* **2010**, *49* (46), 8630−8634. (b) Gassensmith, J. J.; Furukawa, H.; Smaldone, R. A.; Forgan, R. S.; Botros, Y. Y.; Yaghi, O. M.; Stoddart, J. F. Strong and Reversible Binding of Carbon Dioxide in a Green Metal-Organic Framework. *J. Am. Chem. Soc.* **2011**, *133* (39), 15312−15315.

(9) For a recent review of environmental applications of MOFs, particularly with regards to CO_2 capture and sequestration, see: Yaghi, O. M.; Li, Q. Reticular Chemistry and Metal-Organic Frameworks for Clean Energy. *MRS Bull.* **2009**, *34* (9), 682−690.

(10) Wu, D.; Gassensmith, J. J.; Gouvea, D.; Ushakov, S.; Stoddart, J. F.; Navrotsky, A. Direct Calorimetric Measurement of Enthalpy of Adsorption of Carbon Dioxide on CD−MOF-2, a Green Metal-Organic Framework. *J. Am. Chem. Soc.* **2013**, *135* (18), 6790−6793.