Implementation of High School Level Laboratory Experiments Demonstrating Nanoscale Porosity in Metal–Organic Frameworks

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Abstract

Inorganic chemistry draws from many other disciplines of chemistry including organic, analytical, and physical chemistry, making it ideal for teaching foundational topics in high school and introductory undergraduate chemistry curricula. However, students rarely experience modern inorganic materials in introductory classes for a variety of reasons, including complexity of materials synthesis, expense of materials and instrumentation needed to analyze or demonstrate properties, and potential safety concerns. In this study, we use metal–organic frameworks (MOFs) as a modern class of materials that is both emblematic of the interdisciplinary nature of inorganic chemistry and capable of straightforward synthesis and application in introductory chemistry settings. We designed seven laboratory experiences for high school and new undergraduate students that include two MOF syntheses and five follow up gas and solution adsorption experiments. These experiments use low-toxicity reagents and solvents, can be carried out with minimal levels of expertise, and necessitate only common equipment such as laboratory balances and hot plates.

Introduction

Metal–organic frameworks (MOFs) are a class of crystalline materials composed of metal ions or clusters (nodes) and organic ligands (linkers) that have unique properties stemming directly from the connecting geometry of these nodes and linkers.[1] A simplified depiction of MOF construction is shown in Figure 1.

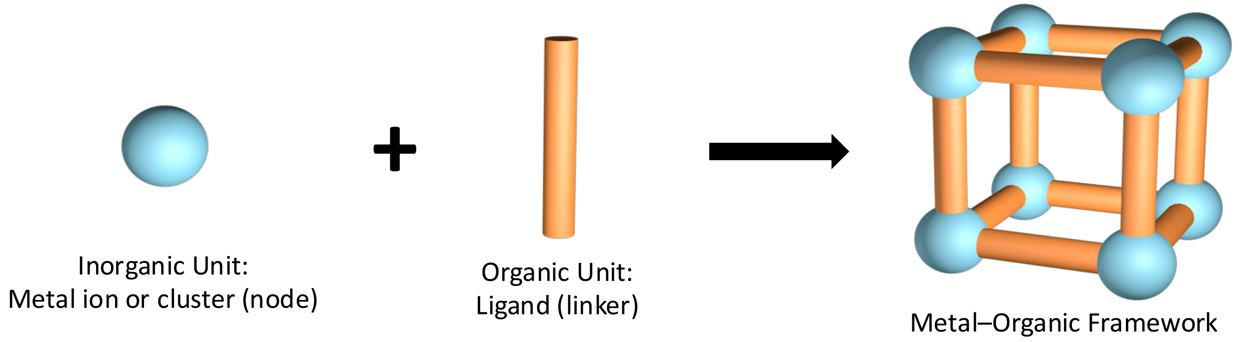


Figure 1. Simplified illustration of MOF construction.

Perhaps the most iconic property of MOFs is their potential porosity. In fact, the IUPAC definition of a MOF is "a coordination network with organic ligands containing potential voids."[2] These voids (pores) range in diameter from approximately 0.3 nm to greater than 2 nm.[3] An example is given in Figure 2, which shows the pores of the MOF $Cu_2(btc)_3$ (commonly termed "HKUST-1"; btc = 1,3,5-benzene tricarboxylate).[4] The presence of empty pores leads to very high internal surface areas (SAs) – MOFs with SA greater than 7000 m^2/g have been reported (approximately the area of 1.3 American football fields!).[5-6] MOFs have the highest surface areas of any known materials.

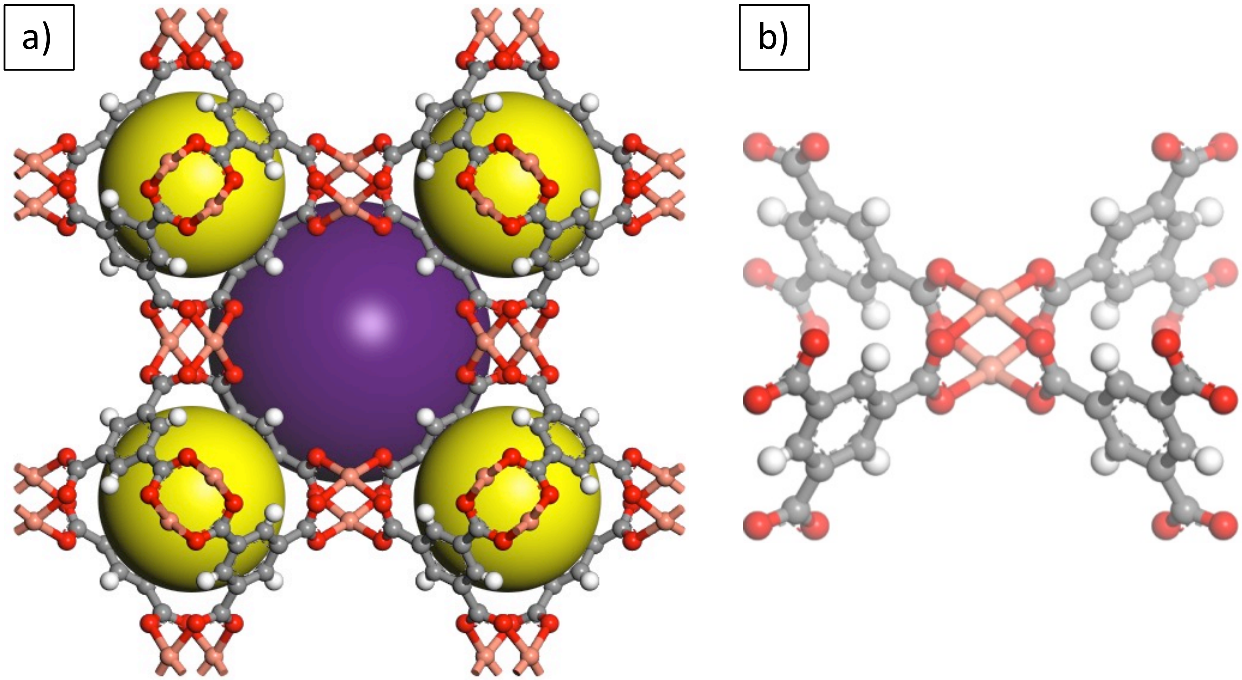


Figure 2. a. Crystallographic model of HKUST-1. Large and small pores are depicted by purple and orange spheres, respectively (Cu, orange; O, red; C, gray; H, white). b. Detail of copper paddlewheel cluster, including surrounding linkers, present in HKUST-1.

The high internal SA of many MOFs allows them to adsorb large amounts of liquids and gases. This characteristic enables the use of MOFs in a wide variety of applications[7] including gas storage and release, chemical separation, catalysis, drug delivery, energy conversion, and sensing.[8] Two particularly important applications (to be discussed in more detail below) are the use of MOFs for removing toxic chemicals from water[9-11] and the capture of carbon dioxide gas.[12-16]

There are more than 115,000 MOFs in the Cambridge Structural Database (CSD) as of March 2023,[17-18] evidence of the enormous and ongoing academic research output in this field.[19-20] Despite the fierce pace of research activity, there are few experiments suitable for students just beginning their studies in chemistry (e.g., high school or early undergraduate students) that provide familiarity with and an understanding of the synthesis and properties of MOFs.[21-25]

Many of the MOF-based experiments published for educational purposes are designed for upper-level undergraduate courses[21, 23, 26-30] and necessitate the use of hazardous reagents and specialized equipment. Hence, these experiments may be inaccessible to high school and lower-level undergraduate laboratories, especially those located in institutions that do not focus heavily on scientific research (such as liberal arts or community colleges). For example, avoiding exposure to chemical hazards such as toxic solvents and reagents are of prime importance in such introductory classroom environments. However, the synthesis of MOFs typically requires harsh solvents such as N,N-dimethylformamide[21, 28, 31-33] or N,N-diethylformamide,[21] necessitating ready access to fume hoods.[34] Rinsing and activation protocols necessary to reveal porosity in MOFs have also required toxic solvents such as chloroform[21] dichloromethane,[21, 23, 27] or tetrahydrofuran.[35] The synthesis of MOFs also requires time; typical solvothermal methods require incubation at elevated temperature for at least 12 hours.[36-37] In contrast, the time allotted for a chemistry lab varies, 2-4 hours at the undergraduate level and 1-1.5 hours at the high school level are typical, for example, in the United States.[4] To our knowledge, with one notable exception,[32] previous reports discussing the use of MOFs for student laboratory exercises employ synthesis methods requiring a minimum of 3 hours, not including activation, and some syntheses necessitate incubation overnight or longer.[21-24, 26-29, 31, 33, 35, 38] Furthermore, standard characterization of MOFs requires expensive instruments that are unavailable in most high school and undergraduate classrooms. Previously published articles have recommended characterization using powder X-ray diffraction (PXRD),[21-22, 24, 26-30, 32-35, 38-39] gas sorption analysis,[21-22, 27-28, 33] Fourier-transform infrared spectroscopy (FTIR),[29-30, 32-35, 38-39] Raman spectroscopy,[33] nuclear magnetic resonance spectroscopy,[21, 30-31, 35] thermogravimetric analysis,[21-22, 26-30, 32-35, 39] differential scanning calorimetry,[22] and gas chromatography–mass spectrometry;[35] all of these instruments cost tens or hundreds of thousands of US dollars (excepting some inexpensive, low resolution FTIR instruments). As has recently been recognized,[24-25] exploring and understanding the properties of MOFs by high school and undergraduate students at under- and moderately-resourced institutions must be accomplished by avenues that do not require the use of such expensive equipment.

Herein we introduce synthesis and adsorption experiments appropriate for high school and undergraduate laboratory settings that overcome the three major challenges outlined above: avoiding hazardous chemicals, time constraints, and lack of sophisticated and expensive equipment. Furthermore, our experiments were guided by the principles of green chemistry[40] including the use of safe solvents, reagents, and reaction conditions.

First, we have developed new procedures for the syntheses of two well-known and well-studied MOFs, HKUST-1[37] and aluminum fumarate (AlF).[41] These procedures are rapid, use reagents and solvents of low toxicity, and require synthetic equipment no more sophisticated than a hot plate and (optionally) a vacuum pump or other source of reduced pressure (e.g., a water aspirator pump). The first synthesis of HKUST-1 published for educational purposes required 48 hours, followed by a drying time of 12 hours.[21] A more recent report disclosed an ultrasonic-assisted synthesis reaching 45-60% yield in just 15 minutes, albeit requiring an ultrasonic cleaner and DMF.[32] In our approach, approximately 70 minutes are needed for MOF synthesis, washing, and drying. The previously reported 3 hours required to synthesize AlF was reduced to 1 hour by minor modification to the published procedure.[42] Furthermore, the previously published synthesis protocols have required toxic solvents, typically dichloromethane and DMF.[21, 31, 38] Here, we use only water and absolute ethanol as solvents (noting that isopropanol can be used in place of ethanol where the latter is not available, albeit resulting in somewhat lower quality material).

Second, we designed two experiments that demonstrate the porosity of MOFs without resorting to prohibitively expensive or complex tools. As early as 1949 the Journal of Chemistry Education published a teacher demonstration of gas adsorption using activated charcoal, activated alumina, and silica gel.[43] More recently, in 2014, Cheung published teacher demonstrations to show gas adsorption using zeolites.[44] Inspired to not only demonstrate gas adsorption using MOFs, but also to provide a safe, hands-on experiment for students to perform for themselves, we developed a procedure that allows students to *quantify* the amount of CO_2 gas their synthesized MOFs adsorb using a standard laboratory balance. This simple procedure can be completed in less than 1 hour, and the effectiveness of each MOF for adsorbing CO_2 can be compared. In a second adsorption experiment, students use the synthesized MOF for adsorption of aqueous methylene blue dye and aqueous potassium iodide and iodine. The only instrumentation necessary for the liquid adsorption experiments is a smartphone that can access Google Play (phones running Android OS).

The synthesis and adsorption experiments are summarized in Figure 3. They are designed to provide teachers with the flexibility to implement them in parts or in whole. The approximate amount of time needed to complete each synthesis and dry each material (70 and 120 minutes for HKUST-1 and AlF, respectively) is shown. However, these times can be reduced by omitting the >45 minute drying steps and instead storing the synthesized MOF(s) at 85 °C until the subsequent lab session. Detailed procedures for each lab are provided in the Supporting Information.

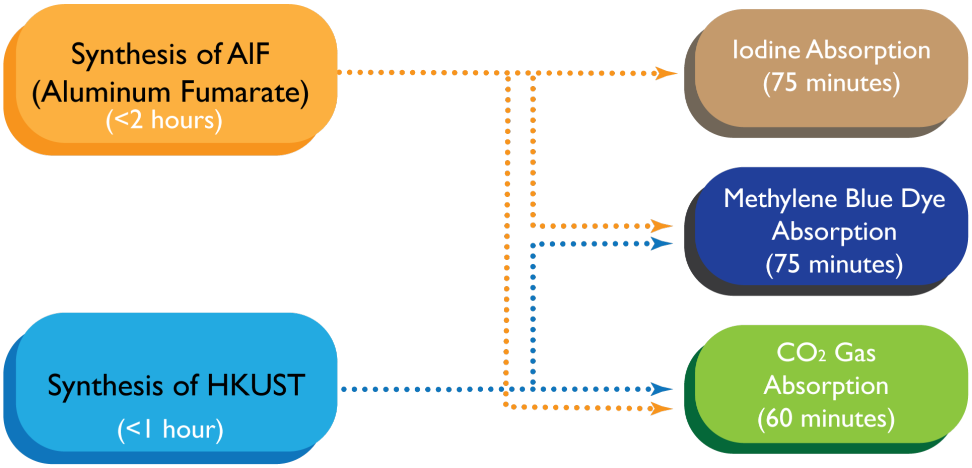


Figure 3. Schematic overview of experiments designed for high school and introductory undergraduate laboratory settings, with approximate time required for each experiment.

These lab experiments support learning concepts including properties of gases, ideal gas law, states of matter, phase transitions, density, inorganic materials synthesis, carbon and its compounds, the carbon cycle, applications of chemistry, solutions, molarity, units and measurements, the electromagnetic spectrum, and spectrophotometers. An additional benefit is the use of Excel for data recording, graphing, and calculations, thus providing students exposure to and experience with computer software for analyzing experimental data.

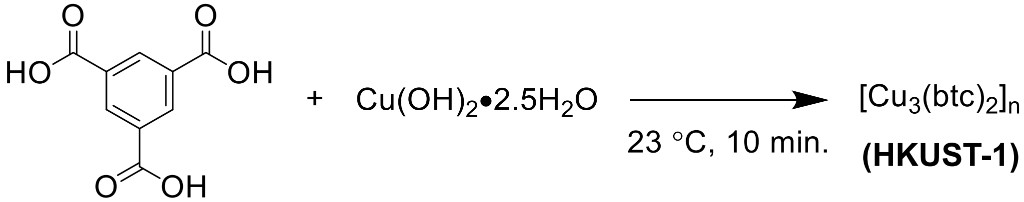
Hazards

We have focused here on making the experiments as safe as possible. However, students should wear standard personal protective equipment such as lab aprons/coats, safety goggles, and disposable latex or nitrile gloves. Students should use caution around hot plates. The ethanol waste produced from the synthesis experiments (used for washing the MOF(s)) may also contain unreacted reagents as well as the MOFs themselves. This waste should be disposed of in accordance with local laws. Students should use caution to not touch the solid CO_2 pellets, and to hold the plastic bottle at the neck of the bottle (not at the bottom) to avoid frostbite on extended contact with skin.

Results and Discussion

Synthesis of HKUST-1

HKUST-1 (Scheme 1), first reported in 1999 by Chui *et al.*,[37] is one of the most widely studied MOFs due to its high surface area, large pore volume, and relative ease of synthesis and handling.[45] Its structure, depicted in Figure 2, consists of inorganic copper "paddlewheel" clusters linked by the organic ligand btc (Figure 2b).[37] It is conventionally synthesized by heating a mixture of DMF, ethanol, water, $Cu(NO_3)_2$, H_3btc, and a small amount of concentrated HCl (which improves the quality of the material) at 85 °C under autogenous pressure for approximately 16-20 h.[10, 46] Given the toxicity of DMF, the corrosive nature of concentrated HCl, and the time required by this synthetic method, we developed an approach more conducive for high school and early undergraduate classrooms. In our process, $Cu(OH)_2$ is mixed with the linker (H_3btc) in a mixture of water and ethanol for ~10 minutes at room temperature and atmospheric pressure (see the Supporting Information). The resulting blue precipitate (Figure S1a) can be rinsed with ethanol and dried for 45 minutes in a drying oven at held at 85 °C, after which it is ready for subsequent adsorption experiments. Consistent with previous reports, a color change from light blue to deep blue occurs upon drying.[47-48]



Scheme 1. Synthesis of HKUST-1 described in this work.

The HKUST-1 produced by our method was characterized by PXRD and gas sorption to ensure this MOF was of suitable quality for student-led adsorption experiments. *We emphasize that characterization by these methods is not part of the classroom experiments that are the focus* *of this report* and is included here only to assess the efficacy of our modified synthesis. The measured PXRD pattern for HKUST-1 shows good agreement with that simulated from the crystallographic model[37] (Figure S1b). The broad reflections at $2\theta = 16.56°$, 23.7°, 33.99°, 36.06°, 38.01°, and 39.86° can be attributed to copper hydroxide impurities generated during the synthesis of the MOF.[49] These copper oxide impurities are not unexpected given the high water content of the solvent mixture used to synthesize the material, as well as exposure to ambient conditions during drying.[50-51] The BET surface area[52] of the HKUST-1 sample was determined by N_2 gas adsorption at 77 K (Figure S1c). The sample was activated at 65 °C for 15 h under reduced pressure (~50 mTorr) prior to analysis. The BET surface area was measured to be 1434 m^2/g, typical for HKUST-1,[45] albeit lower than the theoretical value of 2153 m^2/g.[53] The reduced surface area relative to expectation from the pristine crystallographic model is not surprising given the evidence for non-porous copper hydroxide impurities in the PXRD pattern, which would reduce the overall surface area of the sample. However, this surface area shows that approximately 75% of the pores are still open and accessible, making this HKUST-1 appropriate for demonstrating porosity in the experiments described below.

Synthesis of AlF

AlF was first reported in a patent in 2009 by Kiener, Müller, and Schubert.[54] It is a particularly important MOF due to its excellent chemical stability (including water stability),[26, 41] low production cost, and the fact that it is made from relatively non-toxic and inexpensive reagents. It is one of the few MOFs to date that has achieved commercial success.[55] Also sold under the trademark name Basolite A520, this MOF has been studied for use in the automotive industry as a sorbent to store and deliver natural gas[41] and as a sorbent for ethylene gas for fresh produce packaging.[56] AlF is permanently porous[42] and contains square channel pores (Figure 4a). The framework consists of infinite -Al-OH-Al- chains connected by fumarate linkers[57] (Figure 4b).

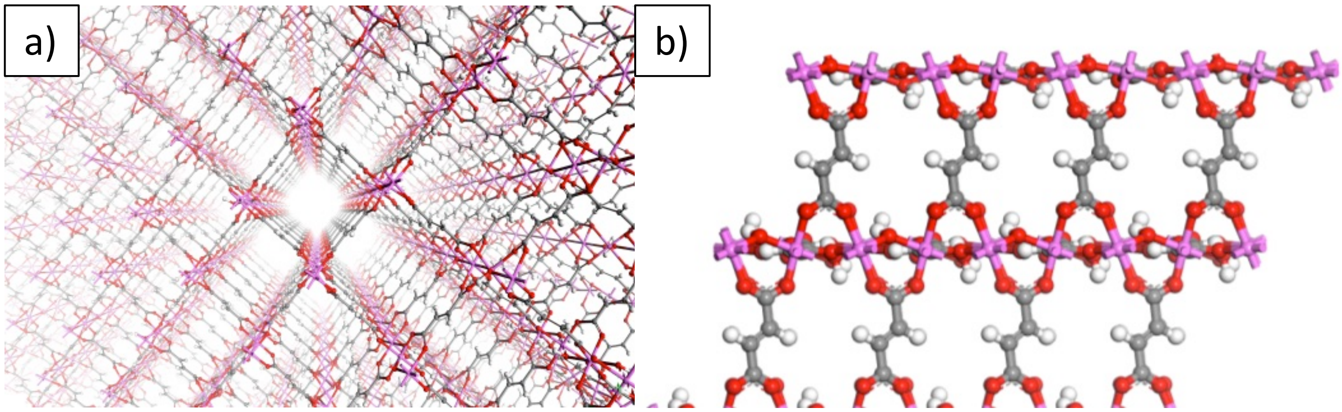
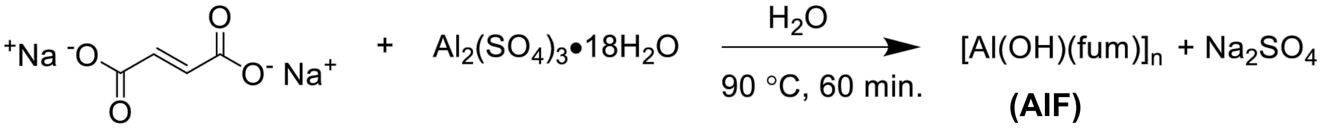


Figure 4. a) Crystallographic model oriented along the crystallographic *c*-axis showing the square channel pores of AlF. b) Crystallographic model viewed perpendicular to the (011) plane showing the infinite -OH-Al-OH-Al- chains in AlF.

Our synthesis method (Scheme 2) is a modified version of that used by Karmaker *et al.*[42] Due to its water stability as well as the solubility of the linker, AlF can be synthesized using only distilled water as the solvent. Aqueous metal salt and fumaric acid solutions are mixed and heated at 90 °C on a hot plate for approximately 1 hour, during which time a white precipitate forms (Figure S2a). The MOF is then washed with ethanol and dried at 85 °C for 45 minutes. In addition to the environmentally friendly and safe synthesis protocol, only 2 hours are needed to prepare the activated (dry) material, important to accommodate the time constraints of a typical high school or undergraduate laboratory setting.



Scheme 2. Synthesis of AlF described in this work.

Analysis by PXRD shows reasonable agreement between experimental data and that simulated from the crystallographic model (Figure S2b). We attribute the broader peaks in the experimental data to small crystallite size.[58] The origin of the difference of 0.1° in 2θ in the lowest angle reflection is not clear, but does not substantially interfere with the materials' porosity or stability. N_2 gas sorption analysis at 77 K after activation at 150 °C for 22 hours revealed the expected type I isotherm (Figure S2c). The BET surface area was determined to be 1091 m^2/g, only slightly lower than the optimized value of 1156 m^2/g obtained by Karmakar *et al*.[42, 59-61] Hence, the preparation of AlF described herein is an effective way to obtain this porous MOF for classroom experiments.

Laboratory Experiments to Demonstrate Adsorption by MOFs

To demonstrate the porosity of HKUST-1 and AlF in a typical classroom setting, two experiments were developed. The first is an integrative exercise incorporating the concepts of solute adsorption by porous materials and visible light absorption spectroscopy.[62] The other is a quantitative and visual experiment demonstrating gaseous CO_2 adsorption.

Adsorption of Aqueous Methylene Blue Dye and Iodine/ Potassium Iodide

With nearly 8 billion people in the world, access to clean water is of paramount importance[63] and water pollution is a global threat.[64] Dyes, which are ubiquitous in nearly every manufacturing industry (e.g. paper, plastics, textiles, food, medication, etc.) have become a significant class of water pollutants. Many dyes undergo chemical changes in wastewater and are not easily degradable. These chemical transformations yield compounds that are harmful, significantly contributing to poor water quality that often proves fatal for aquatic life due to depleted oxygen availability.[10] One solution to this problem is to remove the chemical pollutants by adsorption. MOFs are excellent candidates for dye adsorption given their high accessible internal surface areas. In this set of experiments, students monitor the concentration of a solution of methylene blue or Lugol's solution,[65] an aqueous solution prepared from water, I_2, and KI, as the solute adsorbs to the MOF powder. The previously published work of Kuntzleman *et al*.[66] describes a method by which a smartphone app can be used to teach Beer's Law and explore concepts and equations involved in absorption spectrometry. Taking inspiration from this work, we used this smart phone app to determine the color intensity of a solution as dye is adsorbed on to a MOF, allowing quantification of the amount of dye adsorbed. We note also a recent report in which the MOFs MOF-5, ZIF-8, and MIL-101(Fe) were used to adsorb I_2 from methanol.[24] The first step in the dye adsorption experiments requires setting up an apparatus for using a smart phone colorimeter app as shown in Figure 5.

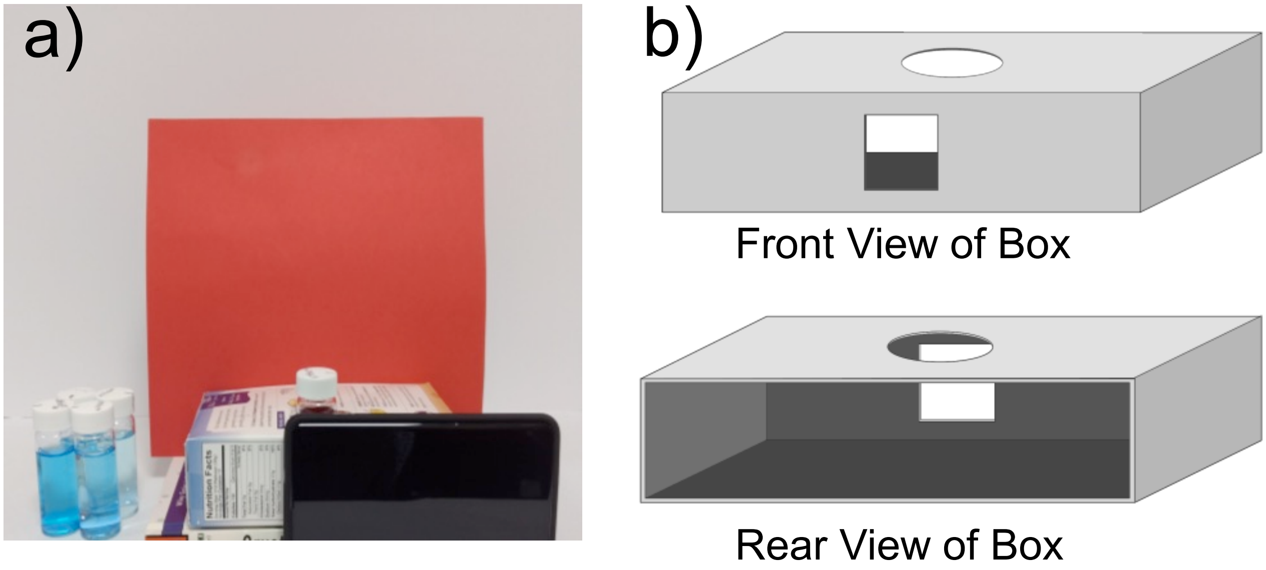
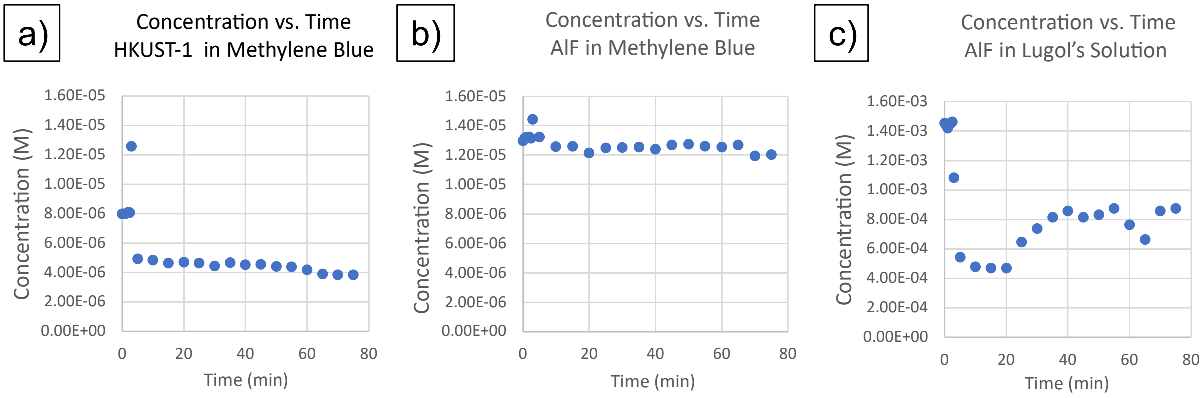


Figure 5. a) Colorimeter and cell phone apparatus for solution adsorption experiments. b) Schematics showing construction of the colorimeter apparatus.

Detailed descriptions are provided in the Supporting Information. The measurement apparatus is a modified version of that described previously.[66] A hole just large enough to fit the vial containing the dye solution is cut into the top surface of a cardboard box. A second, smaller hole is cut into one of the sides of the box to accommodate visualization with a smart phone camera. The opposite side of the box is cut away completely and is replaced with a piece of colored stock paper. Once the measurement apparatus is constructed, it can be stored and used indefinitely. However, during data collection, the apparatus must remain stationary, a feat straightforward to accomplish with tape. The cell phone should not be moved once positioned and the ambient light in the room should remain constant during the course of the measurement, as changes in lighting conditions can introduce systematic error.

The free Google Play colorimeter app *Color Meter* is used to monitor the change in concentration of dye as the dye is adsorbed by the MOF. *Color Meter* conducts a colorimetric analysis of images produced by the cellphone's camera, yielding red, green and blue values. The number read and recorded (red, blue or green) corresponds to the intensity of the color that is closest to that *absorbed* by the solution. Hence, higher numbers correspond to lower absorption of light by the solution. The recorded intensity can be related to solution concentration by Beer's Law, where the absorbance values are plotted against known concentrations of prepared solutions in a calibration curve. Dye adsorption is carried out by first constructing these calibration curves as described in detail in the Supporting Information. These can be constructed by the instructor prior to the lesson or by students during class. Student can also prepare solutions for calibration, depending on the experience and expertise of the students as well as the available time for the laboratory experiment. To measure dye adsorption by a MOF, a vial containing an aqueous dye solution is first inserted into the colorimeter apparatus. The appropriate pre-adsorption colorimeter value (red, green, or blue, depending on the dye; see the Supporting Information) is measured several times over several minutes to ensure a repeatable value is recorded. MOF is then added to the solution and the cellphone is immediately used to record changes in the appropriate color value occurring as a result of dye being adsorbed by the MOF. For example, HKUST-1 can be used to adsorb methylene blue, removing it from the aqueous phase. Since methylene blue absorbs red light, the dye's removal from solution in this case would increase the red value read by *Color Meter*. For all dye adsorption experiments, students can record color values as time allows, but adsorption is typically observable within the first 15 minutes. Figure 6a shows representative data of methylene blue adsorption by HKUST-1. Although methylene blue is relatively large, having rectangular dimensions of approximately 17.0 Å × 7.6 Å × 3.3 Å,[67] its smaller dimensions (7.6 Å × 3.3 Å) allow it to be removed from solution by HKUST-1, which has a pore diameter of approximately 11 Å (for the larger, interconnected pores).[37] In contrast, due to its smaller pore diameter (5.7-6 Å),[54] AlF shows negligible methylene blue dye adsorption (Figure 6b). Students can use these experiments to directly measure the consequences of pore size on guest adsorption in MOFs. Optionally, students can also measure the adsorption of iodine species by AlF; although iodine exists in Lugol's solution as a complex mixture of species, predominant species (I^-, I_2, and I_3^-)[65] are small enough to be adsorbed by this MOF (Figure 6c). We note that HKUST-1 degrades in Lugol's solution; a comparison of adsorption capacity of the two MOFs can be achieved by the CO_2 gas adsorption experiment described below. To quantify dye adsorption, Microsoft Excel© is used to construct a calibration curve, record data, calculate concentration changes, and plot results. Detailed instructions are provided in Supporting Information.



HKUST-1 / Methylene Blue AlF / Methylene Blue AlF / Lugol's Solution

Figure 6. Concentration of aqueous colorant *vs*. time after addition of HKUST-1 or AlF. Data collected with the *Color Meter* app, and figures were made using Excel as described in the Supporting Information.

Carbon Dioxide Gas Adsorption Experiments

The sequestration of atmospheric CO_2 is one of the most pressing challenges of our time.[68] MOFs have demonstrated extraordinarily high gas capture capacities – the highest, in fact, among all known adsorbents.[14]

In this experiment, students directly assess the effectiveness of their MOFs for CO_2 uptake under ambient conditions. Figure 7 illustrates the steps of the procedure. First, a plastic bottle is filled with dry ice. As the dry ice sublimes, gaseous CO_2 displaces the air in the bottle. A balloon is then placed over the plastic bottle and allowed to fill with CO_2 gas generated by the dry ice. The CO_2-filled balloon is then placed tightly over an empty vessel and allowed to remain in place for approximately 15 minutes. This ensures that most of the air present in the vessel is displaced with CO_2 gas as it is more dense than air. The balloon is then removed, and the MOF is quickly added to the vial which is then capped and re-weighed. After the initial mass of MOF before adsorption is recorded, the balloon is again secured to the vessel and left for 30 minutes to allow the MOF to adsorb the CO_2 gas. After 30 minutes, the balloon is removed and the vessel is recapped and immediately weighed to determine the extent of CO_2 adsorption. Each adsorption experiment can be completed in less than 1 hour.

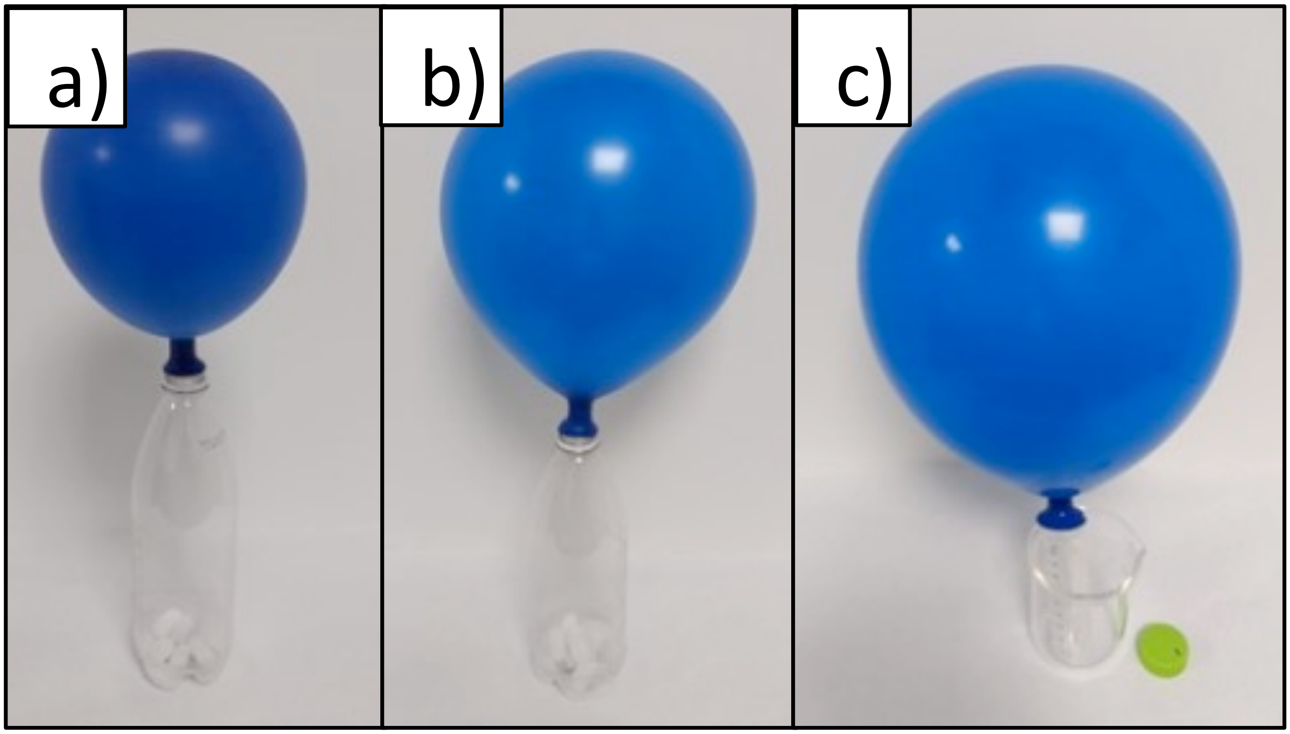


Figure 7. Photographs of balloon a) prior to and b) following collection of CO2(g) from subliming dry ice. c) Photograph of MOF sample in a vessel attached to the CO_2 balloon for gas adsorption.

An example of representative CO_2 adsorption data is shown in Tables S1 and S2. Students use the ideal gas law to quantify the amount of CO_2 adsorbed (see the example calculation given in the Supporting Information). HKUST-1 and AlF adsorb approximately 1.0 and 0.7 mmol CO_2/g MOF, respectively. These values are in agreement with the expectation that HKUST-1 should have higher CO_2 uptake than AlF.[69-70] In these CO_2 adsorption experiments, it is important to recognize that the capacity for the MOFs to adsorb CO_2 is due not only to pore size, surface area, and volume, but also to experimental factors such as temperature and humidity.[10, 37] Finally, we note that sand or table salt can be used as non-porous controls; they do not adsorb measurable amounts of CO_2 when used in place of a MOF in an otherwise identical experiment.

Summary

The experiments described herein provide students exposure to and hands-on experience with MOFs – a topic that has received only modest attention in a format amenable to adoption by high school and lower-level college classes. Students learn and practice laboratory skills as they synthesize two widely-studied MOFs. Students see first-hand the potential for MOFs as adsorbents by using their synthesized MOF(s) to adsorb methylene blue dye, aqueous iodine/iodide, and CO_2 gas. The MOFs are easy to synthesize, the chemicals are safe to use, and the procedures are designed for a level of complexity appropriate for students in their first or second chemistry course. After synthesis, the adsorption experiments can be performed as stand-alone labs, allowing teachers flexibility for how they can use the experiments described herein. Student's knowledge and recollection of chemistry concepts is encouraged and strengthened. Finally, new learning is stimulated with unfamiliar topics including MOFs, porosity, surface area, crystallinity, and inorganic chemistry.

References

1. Seth, S.; Matzger, A. J., Metal–Organic Frameworks: Examples, Counterexamples, and an Actionable Definition. *Cryst. Growth Des.* **201,** *17* (8), 4043-4048.

2. Batten, S.; Champness, N.; Chen, X.-M.; García-Martínez, J.; Kitagawa, S.; Öhrström, L.; O Keeffe, M.; Suh, M.; Reedijk, J., *Terminology of Metal–Organic Frameworks and Coordination Polymers (IUPAC Recommendations 2013)**. 2013; Vol. 85, p 1715-1724.

3. Ongari, D.; Boyd, P. G.; Barthel, S.; Witman, M.; Haranczyk, M.; Smit, B., Accurate Characterization of the Pore Volume in Microporous Crystalline Materials. *Langmuir* **2017,** *33* (51), 14529-14538.

4. Irmsher, K., Block Scheduling *ERIC Digest* **1996,** *104* (ED393156).

5. Farha, O. K.; Eryazici, I.; Jeong, N. C.; Hauser, B. G.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Nguyen, S. T.; Yazaydın, A. Ö.; Hupp, J. T., Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? *J. Am. Chem. Soc.* **2012,** *134* (36), 15016-15021.

6. Hönicke, I. M.; Senkovska, I.; Bon, V.; Baburin, I. A.; Bönisch, N.; Raschke, S.; Evans, J. D.; Kaskel, S., Balancing Mechanical Stability and Ultrahigh Porosity in Crystalline Framework Materials. *Angew. Chem., Int. Ed.* **2018,** *57* (42), 13780-13783.

7. Yuan, S.; Zou, L.; Qin, J.-S.; Li, J.; Huang, L.; Feng, L.; Wang, X.; Bosch, M.; Alsalme, A.; Cagin, T.; Zhou, H.-C., Construction of Hierarchically Porous Metal–Organic Frameworks Through Linker Labilization. *Nat. Commun.* **2017,** *8*, 15356.

8. Kuppler, R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J.-R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.-C., Potential Applications of Metal-Organic Frameworks. *Coordination Chemistry Reviews* **2009,** *253* (23), 3042-3066.

9. Howarth, A. J.; Liu, Y.; Hupp, J. T.; Farha, O. K., Metal–Organic Frameworks for Applications in Remediation of Oxyanion/Cation-Contaminated Water. *CrystEngComm* **2015,** *17* (38), 7245-7253.

10. Kaur, R.; Kaur, A.; Umar, A.; Anderson, W. A.; Kansal, S. K., Metal Organic Framework (Mof) Porous Octahedral Nanocrystals of Cu-Btc: Synthesis, Properties and Enhanced Adsorption Properties. *Mater. Res. Bull.* **2019,** *109*, 124-133.

11. Gao, Q.; Xu, J.; Bu, X.-H., Recent Advances About Metal–Organic Frameworks in the Removal of Pollutants from Wastewater. *Coord. Chem. Rev.* **2018,** *378*.

12. Ding, M.; Flaig, R. W.; Jiang, H.-L.; Yaghi, O. M., Carbon Capture and Conversion Using Metal–Organic Frameworks and Mof-Based Materials. *Chem. Soc. Rev.* **2019,** *48* (10), 2783-2828.

13. Wang, B.; Xie, L.-H.; Wang, X.; Liu, X.-M.; Li, J.; Li, J.-R., Applications of Metal–Organic Frameworks for Green Energy and Environment: New Advances in Adsorptive Gas Separation, Storage and Removal. *GEE* **2018,** *3* (3), 191-228.

14. Trickett, C. A.; Helal, A.; Al-Maythalony, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M., The Chemistry of Metal–Organic Frameworks for CO_2 Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017,** *2*, 17045.

15. Adeyemo, A. A.; Adeoye, I. O.; Bello, O. S., Metal Organic Frameworks as Adsorbents for Dye Adsorption: Overview, Prospects and Future Challenges. *Toxicol. Environ. Chem.* **2012,** *94* (10), 1846-1863.

16. Liu, Y.; Wang, Z. U.; Zhou, H.-C., Recent Advances in Carbon Dioxide Capture with Metal-Organic Frameworks. *GREENH GASES* **2012,** *2* (4), 239-259.

17. Moghadam, P. Z.; Li, A.; Liu, X.-W.; Bueno-Perez, R.; Wang, S.-D.; Wiggin, S. B.; Wood, P. A.; Fairen-Jimenez, D., Targeted Classification of Metal–Organic Frameworks in the Cambridge Structural Database (CSD). *Chem. Sci.* **2020,** *11* (32), 8373-8387.

18. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C., The Cambridge Structural Database. *Acta Crystallographica Section B* **2016,** *72* (2), 171-179.

19. Wang, C.-C.; Ho, Y.-S., Research Trend of Metal–Organic Frameworks: A Bibliometric Analysis. *Scientometrics* **2016,** *109* (1), 481-513.

20. Ogawa, T.; Iyoki, K.; Fukushima, T.; Kajikawa, Y., Landscape of Research Areas for Zeolites and Metal-Organic Frameworks Using Computational Classification Based on Citation Networks. *MATLS* **2017,** *10* (12), 20.

21. 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.

22. Wriedt, M.; Sculley, J. P.; Aulakh, D.; Zhou, H.-C., Using Modern Solid-State Analytical Tools for Investigations of an Advanced Carbon Capture Material: Experiments for the Inorganic Chemistry Laboratory. *J. Chem. Educ.* **2016,** *93* (12), 2068-2073.

23. Smith, M. K.; Angle, S. R.; Northrop, B. H., Preparation and Analysis of Cyclodextrin-Based Metal–Organic Frameworks: Laboratory Experiments Adaptable for High School through Advanced Undergraduate Students. *J. Chem. Educ.* **2015,** *92* (2), 368-372.

24. Sakamaki, Y.; Tsuji, M.; Heidrick, Z.; Watson, O.; Durchman, J.; Salmon, C.; Burgin, S. R.; Beyzavi, M. H., Preparation and Applications of Metal–Organic Frameworks (MOFs): A Laboratory Activity and Demonstration for High School and/or Undergraduate Students. *J. Chem. Educ.* **2020**.

25. Benedetto, G.; Cleary, B. M.; Morrell, C. T.; Durbin, C. G.; Brinks, A. L.; Tietjen, J.; Mirica, K. A., CD-MOF-1 for CO2 Uptake: Remote and Hybrid Green Chemistry Synthesis of a Framework Material with Environmentally Conscious Applications. *J. Chem. Educ.* **2023,** *100* (3), 1289-1295.

26. Crane, J. L.; Anderson, K. E.; Conway, S. G., Hydrothermal Synthesis and Characterization of a Metal–Organic Framework by Thermogravimetric Analysis, Powder X-ray Diffraction, and Infrared Spectroscopy: An Integrative Inorganic Chemistry Experiment. *J. Chem. Educ.* **2015,** *92* (2), 373-377.

27. Lyle, S. J.; Flaig, R. W.; Cordova, K. E.; Yaghi, O. M., Facilitating Laboratory Research Experience Using Reticular Chemistry. *J. Chem. Educ.* **2018,** *95* (9), 1512-1519.

28. Yuan, M.; Sun, C.-Y.; Liu, Y.-W.; Lu, Y.; Zhang, Z.; Li, X.-H.; Tian, H.-R.; Zhang, S.; Liu, S.-X., Synthesis, Characterization, and Property Investigation of a Metal–Organic Framework Encapsulated Polyoxometalate Guests: An Advanced Inorganic Chemistry Experiment. *J. Chem. Educ.* **2020,** *97* (11), 4152-4157.

29. Gao, Z.; Lai, Y.; Zhang, L.; Lin, Y.; Xiao, L.; Luo, Y.; Luo, F., Synthesis, Characterization, and Electrocatalytic Activity Exploration of MOF-74: A Research-Style Laboratory Experiment. *J. Chem. Educ.* **2021,** *98* (10), 3341-3347.

30. VanOursouw, T. M.; Rottiger, T.; Wadzinski, K. A.; VanderWaal, B. E.; Snyder, M. J.; Bittner, R. T.; Farha, O. K.; Riha, S. C.; Mondloch, J. E., Adsorption of a PFAS Utilizing MOF-808: Development of an Undergraduate Laboratory Experiment in a Capstone Course. *J. Chem. Educ.* **2023,** *100* (2), 861-868.

31. 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.

32. Liu, Y.; Myers, E. J.; Rydahl, S. A.; Wang, X., Ultrasonic-Assisted Synthesis, Characterization, and Application of a Metal–Organic Framework: A Green General Chemistry Laboratory Project. *J. Chem. Educ.* **2019**.

33. Panda, D.; Patra, S.; Awasthi, M. K.; Singh, S. K., Lab Cooked MOF for CO_2 Capture: A Sustainable Solution to Waste Management. *J. Chem. Educ.* **2020**.

34. Cheng, Y.; Shi, D.; Di Yuan, Y.; Zhao, D., Facile Synthesis of a Metal–Organic Framework for Removal of Methyl Blue from Water: First-Year Undergraduate Teaching Lab. *J. Chem. Educ.* **2020,** *97* (11), 4145-4151.

35. Mancheño, M. J.; Royuela, S.; de la Peña, A.; Ramos, M.; Zamora, F.; Segura, J. L., Introduction to Covalent Organic Frameworks: An Advanced Organic Chemistry Experiment. *Journal of Chemical Education* **2019**.

36. Schlichte, K.; Kratzke, T.; Kaskel, S., Improved Synthesis, Thermal Stability and Catalytic Properties of the Metal-Organic Framework Compound $Cu_3(Btc)_2$. *Microporous and Mesoporous Mater.* **2004,** *73* (1), 81-88.

37. Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D., A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H_2O)_3]_n$. *Science* **1999,** *283* (5405), 1148-1150.

38. Yuan, M.; Tang, Q.; Lu, Y.; Zhang, Z.; Li, X.-H.; Liu, S.-M.; Sun, X.-W.; Liu, S.-X., Using the Luminescence and Ion Sensing Experiment of a Lanthanide Metal–Organic

Framework to Deepen and Extend Undergraduates' Understanding of the Antenna Effect. *Journal of Chemical Education* **2019**.

39. Zanotelli, N. C.; Rodrigues, R. V.; de Souza, R. F. F.; de Campos, S. D.; de Campos, É. A., From Metal Complexes to BioMOFs: An Experimental Proposal for Teaching Coordination Chemistry Concepts. *J. Chem. Educ.* **2023,** *100* (2), 844-851.

40. Anastas, P.; Eghbali, N., Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010,** *39* (1), 301-312.

41. Arnold, L.; Averlant, G.; Marx, S.; Weickert, M.; Müller, U.; Mertel, J.; Horch, C.; Peksa, M.; Stallmach, F., Metal Organic Frameworks for Natural Gas Storage in Vehicles. *Chemie Ingenieur Technik* **2013,** *85* (11), 1726-1733.

42. Karmakar, S.; Dechnik, J.; Janiak, C.; De, S., Aluminium Fumarate Metal-Organic Framework: A Super Adsorbent for Fluoride from Water. *J. Hazard. Mater.* **2016,** *303*, 10-20.

43. Blankenship, F.; Conaldson, P., An Improved Demonstration Experiment on Gas Adsorption. *Journal of Chemical Education* **1949,** *26* (2), 105.

44. Cheung, O., Visualizing Gas Adsorption on Porous Solids: Four Simple, Effective Demonstrations. *Journal of Chemical Education* **2014,** *91* (9), 1468-1472.

45. Chen, Y.; Mu, X.; Lester, E.; Wu, T., High Efficiency Synthesis of HKUST-1 Under Mild Conditions with High BET Surface Area and CO_2 Uptake Capacity. *PRO NAT SCI-MATER* **2018,** *28* (5), 584-589.

46. Feldblyum, J. I.; Liu, M.; Gidley, D. W.; Matzger, A. J., Reconciling the Discrepancies between Crystallographic Porosity and Guest Access As Exemplified by Zn-HKUST-1. *J. Am. Chem. Soc.* **2011,** *133* (45), 18257-18263.

47. Doan, H. V.; Fang, Y.; Yao, B.; Dong, Z.; White, T. J.; Sartbaeva, A.; Hintermair, U.; Ting, V. P., Controlled Formation of Hierarchical Metal–Organic Frameworks Using CO_2-Expanded Solvent Systems. *ACS Sustainable Chem. Eng.* **2017,** *5* (9), 7887-7893.

48. Lestari, W.; Adreane, M.; Purnawan, C.; Fansuri, H.; Widiastuti, N.; Rahardjo, S., Solvothermal and Electrochemical Synthetic Method of Hkust-1 and its Methane Storage Capacity. *IOP Conf Ser Mater Sci Eng* **2016,** *107*, 012030.

49. Wyckoff, R. W. G., *Crystal Structures*. 2nd Ed. ed.; Interscience Publishers: New York, New York, 1963; Vol. 1.

50. Cychosz, K. A.; Matzger, A. J., Water stability of microporous coordination polymers and the adsorption of pharmaceuticals from water. *Langmuir* **2010,** *26* (22), 17198-17202.

51. Küsgens, P.; Rose, M.; Senkovska, I.; Frode, H.; Henschel, A.; Siegle, S.; Kaskel, S., Characterization of Metal-Organic Frameworks by Water Adsorption. *Microporous Mesoporous Mater.* **2009,** *120* (3), 325-330.

52. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938,** *60* (2), 309-319.

53. Düren, T.; Millange, F.; Férey, G.; Walton, K. S.; Snurr, R. Q., Calculating Geometric Surface Areas as a Characterization Tool for Metal−Organic Frameworks. *J. Phys. Chem. C* **2007,** *111* (42), 15350-15356.

54. Alvarez, E.; Guillou, N.; Martineau, C.; Bueken, B.; Van de Voorde, B.; Le Guillouzer, C.; Fabry, P.; Nouar, F.; Taulelle, F.; de Vos, D.; Chang, J.-S.; Cho, K. H.; Ramsahye, N.; Devic, T.; Daturi, M.; Maurin, G.; Serre, C., The Structure of the Aluminum Fumarate Metal–Organic Framework A520. *Angew. Chem. Int. Ed.* **2015,** *54* (12), 3664-3668.

55. Rubio-Martinez, M.; Avci-Camur, C.; Thornton, A. W.; Imaz, I.; Maspoch, D.; Hill, M. R., New Synthetic Routes Towards Mof Production at Scale. *Chem. Soc. Rev.* **2017,** *46* (11), 3453-3480.

56. Chopra, S.; Dhumal, S.; Abeli, P.; Beaudry, R.; Almenar, E., Metal-Organic Frameworks Have Utility in Adsorption and Release of Ethylene and 1-Methylcyclopropene in Fresh Produce Packaging. *POSTHARVEST BIOL TEC* **2017,** *130*, 48-55.

57. Jeremias, F.; Fröhlich, D.; Janiak, C.; Henninger, S. K., Water and Methanol Adsorption on Mofs for Cycling Heat Transformation Processes. *New J. Chem.* **2014,** *38* (5), 1846-1852.

58. Scherrer, P., Gottinger Nachrichten. *Math. Phys* **1918,** *2*, 98-100.

59. Tannert, N.; Jansen, C.; Niessing, S.; Janiak, C., Robust Synthesis Routes and Porosity of the Al-Based Metal-Organic Frameworks Al-Fumarate, CAU-10-H and MIL-160. *J. Chem. Soc., Dalton Trans.* **2019,** *48* (9), 2967-2976.

60. Li, S.; Chen, Y.; Pei, X.; Zhang, S.; Feng, X.; Zhou, J.; Wang, B., Water Purification: Adsorption over Metal-Organic Frameworks. *CHINESE J. CHEM* **2016,** *34* (2), 175-185.

61. Kayal, S.; Chakraborty, A.; Teo, B., *Green Synthesis and Characterization of Aluminium Fumarate Metal-Organic Framework for Heat Transformation Applications*. 2018; Vol. 221.

62. Šafranko, S.; Živković, P.; Stanković, A.; Medvidović-Kosanović, M.; Széchenyi, A.; Jokić, S., Designing ColorX, Image Processing Software for Colorimetric Determination of Concentration, To Facilitate Students' Investigation of Analytical Chemistry Concepts Using Digital Imaging Technology. *Journal of Chemical Education* **2019,** *96* (9), 1928-1937.

63. Dias, E. M.; Petit, C., Towards the Use of Metal–Organic Frameworks for Water Reuse: A Review of the Recent Advances in the Field of Organic Pollutants Removal and Degradation and the Next Steps in the Field. *J. Mater. Chem. A* **2015,** *3* (45), 22484-22506.

64. Drout, R. J.; Robison, L.; Chen, Z.; Islamoglu, T.; Farha, O. K., Zirconium Metal–Organic Frameworks for Organic Pollutant Adsorption. *Trends Chem.* **2019,** *1* (3), 304-317.

65. Kaiho, T., Inorganic Iodides. In *Iodine Chemistry and Applications*, 2014; pp 55-73.

66. Kuntzleman, T. S.; Jacobson, E. C., Teaching Beer's Law and Absorption Spectrophotometry with a Smart Phone: A Substantially Simplified Protocol. *Journal of Chemical Education* **2016,** *93* (7), 1249-1252.

67. Arias, M.; López, E.; Nuñez, A.; Rubinos, D.; Soto, B.; Barral, M. T.; Díaz-Fierros, F., Adsorption of Methylene Blue by Red Mud, An Oxide- Rich Byproduct of Bauxite Refining. In *Effect of Mineral-Organic-Microorganism Interactions on Soil and Freshwater Environments*, Berthelin, J.; Huang, P. M.; Bollag, J. M.; Andreux, F., Eds. Springer US: Boston, MA, 1999; pp 361-365.

68. González-Zamora, E.; Ibarra, I. A., CO_2 Capture Under Humid Conditions in Metal–Organic Frameworks. *Materials Chemistry Frontiers* **2017,** *1* (8), 1471-1484.

69. Chen, Y.; Mu, X.; Lester, E.; Wu, T., High efficiency synthesis of HKUST-1 under mild conditions with high BET surface area and CO2 uptake capacity. *Prog. Nat. Sci.* **2018,** *28* (5), 584-589.

70. Coelho, J. A.; Ribeiro, A. M.; Ferreira, A. F. P.; Lucena, S. M. P.; Rodrigues, A. E.; Azevedo, D. C. S. d., Stability of an Al-Fumarate MOF and Its Potential for CO2 Capture from Wet Stream. *Ind. Eng. Chem. Res.* **2016,** *55* (7), 2134-2143.