

Using Modern Solid-State Analytical Tools for Investigations of an Advanced Carbon Capture Material: Experiments for the Inorganic Chemistry Laboratory

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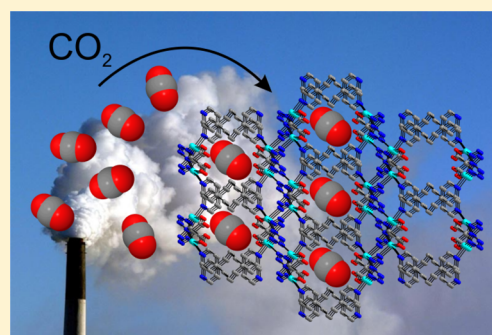
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S Supporting Information

ABSTRACT: A simple and straightforward synthesis of an ultrastable porous metal–organic framework (MOF) based on copper(II) and a mixed N donor ligand system is described as a laboratory experiment for chemistry undergraduate students. These experiments and the resulting analysis are designed to teach students basic research tools and procedures while emphasizing one of the most challenging environmental issues we are facing as a society: reduction of anthropogenic carbon dioxide emissions, and potential technologies that may achieve this. The described experiments take advantage of modern solid-state analytical tools, such as powder X-ray diffraction, thermogravimetric analysis, and gas sorption, to characterize the properties of this particular MOF. The adsorption studies, performed volumetrically and gravimetrically, both have simple experimental setups and enable the students to critically interpret and compare their results. Most importantly, students are required to question structure–property relationships in order to arrive at a full understanding of the selective carbon dioxide capture process. All experiments have been successfully performed with upper-level chemistry undergraduates, preparing them for cutting-edge inorganic and material research topics. The experiments and characterization work can be performed in any combination for which the students have proper equipment and access. The lab was also performed with no experimental equipment, using only the supplemental data files.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Computer-Based Learning, Hands-On Learning/Manipulatives, Coordination Compounds, Solid State Chemistry, Thermal Analysis, Undergraduate Research, X-ray Crystallography



As a society we are facing the grand challenge of mitigating effects of climate change by reducing anthropogenic CO₂ emissions without significantly impacting the costs of energy. Of the many ways this can be achieved, including deployment of renewable energy and storage, efficiency improvements, and carbon capture and storage (CCS), the Intergovernmental Panel on Climate Change (IPCC) and other groups have come to the conclusion that CCS must be part of the mix of solutions.^{1,2} This means that fossil fuel power plants will continue to be a large part of the global energy mix in the majority of future energy scenarios and will need CCS to limit CO₂ emissions. The state of the art technology employed to remove CO₂ from flue gas streams of fossil fuel power plants, amine scrubbing, imposes a huge energy penalty on the power plant.^{3,4} An alternate technology solution, physical adsorbents, comes in various forms ranging from zeolites, to silicas, to metal–organic frameworks (MOFs).^{5–8} MOFs have the unique and advantageous property of being highly tunable via changes in the composition of the metal cluster and/or connecting ligands. Special thematic issues in *Chemical Reviews* and

Chemical Society Reviews provide a more complete picture of the breadth of possible compositions and applications of MOFs.^{9–12} As the chemistry of MOFs is not commonly taught in the undergraduate laboratory setting,^{13–16} we herein present that one particular compound, designated as PCN-200 (PCN = porous coordination network),¹⁷ showing a highly crystalline nature, stability, ease of synthesis, and unique properties, can provide the platform for an interesting student learning experience that offers an understanding of cutting-edge material science and chemistry in the context of the real problem of carbon capture (Figure 1).

This lab offers a broad introduction to CCS, with a specific emphasis on coordination chemistry and modern analytical techniques. Given the importance of climate change mitigation strategies on our future and the benefits of learning by doing, we believe this lab is well-suited for all college-level students.

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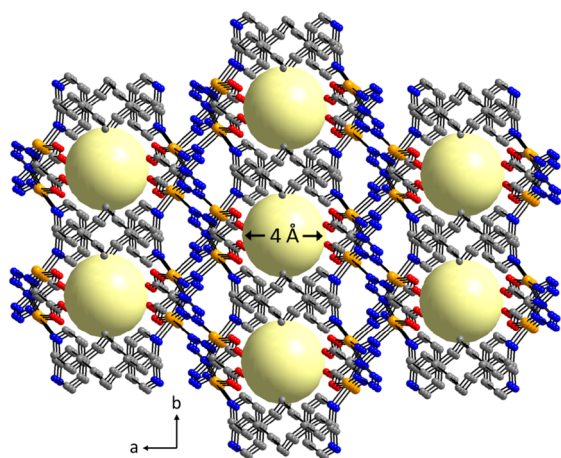


Figure 1. Crystal structure of PCN-200 from single crystal data. Yellow spheres represent guest accessible voids. Hydrogen atoms are omitted for the sake of clarity. Color codes: C, gray; N, blue; O, red; Cu, orange.

The experimental process can easily be tailored to the instruments available in a given lab and tuned to the level of rigor required by the professor. The lab has several subcomponents, including material synthesis, characterization, and analysis, all of which can be performed over three lab sessions (3 h each), or in a one-day lab using the data available in the [Supporting Information](#) as a purely “computational lab”. The experiment described here includes the synthesis of PCN-200 (**1**), and its structural characterization using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gas sorption analysis. The extensive variety of techniques used to characterize this material for purity, thermal properties, and adsorption behavior are typical of chemistry and materials science research, but are unfortunately not commonly used by chemistry undergraduates.^{18–23} We believe exposing students to the multitude of techniques required to carry out science at a research level will help form the basis for problem solving and hypothesis testing skills. Raw data for elemental analysis, PXRD, TGA, and gas adsorption is provided in the [Supporting Information](#) and can either be used as a tool for comparison, or, in the absence of the appropriate instruments, can be used as the “raw data” to perform various calculations and analysis.

■ EXPERIMENTAL OVERVIEW

The experiment described herein emphasizes the simplicity of MOF synthesis and characterization using modern solid-state analytical tools, while demonstrating the potential to be used as a carbon capture material. From a practical viewpoint, this experiment is appealing because the MOF can be easily prepared from inexpensive, commercially available reactants, following a straightforward synthetic route. The preparation and investigation of this MOF can be divided into three stages: (i) synthesis; (ii) purity characterization; and (iii) adsorption properties. Each of the three stages can be tailored according to particular laboratory environments and available instrumentation. The results are more pronounced and favor reproducibility when carried out over a period of three lab sessions ranging between 2 to 3 h each.

Stage one of the experiment involves preparation of **1** from the reaction of an aqueous mixture of copper(II) acetate and 1H-tetrazole-5-carboxylic acid ethyl ester sodium salt (NaEttz)

with 0.5 equiv of 1,3-di(4-pyridyl) propane (dpp) added in several portions with continuous stirring over a period of 30 min. The reaction is performed on a hot plate using a capped scintillation vial maintained at 100 °C overnight. The resulting compound crystallizes as a blue polycrystalline powder of composition $\{[\text{Cu}(\text{tzc})(\text{dpp})_{0.5}]\cdot 1.5\text{H}_2\text{O}\}_n$ (**Figure 2**). Students

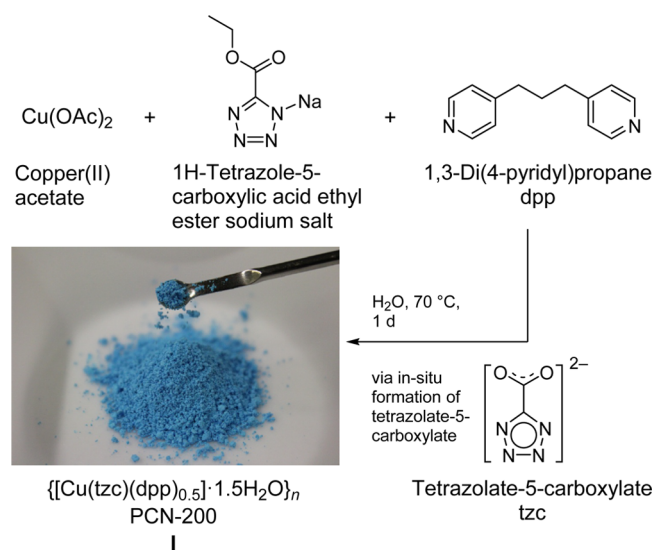


Figure 2. Reaction pathway showing in situ formation of tetrazolate-5-carboxylic acid during MOF synthesis.

should be advised that it is crucial to add the dpp ligand in small portions (crystal by crystal); otherwise, it is likely that the magnetic stir bar will stick to the bottom of the glass vial, resulting in the formation of a nonporous MOF of composition $\{[\text{Cu}(\text{tzc})(\text{dpp})]\cdot 2\text{H}_2\text{O}\}_n$.²⁴ Alternatively, this reaction can be performed in a regular round-bottom flask while heating under reflux. The material is stable in the mother liquor and ambient air until students are able to resume the studies. The crystalline product is isolated by vacuum filtration with typical yields ranging from 95% to 100%.

During stage two of the lab, the students are introduced to various solid-state analytical techniques that are used to confirm the phase purity of the synthesized MOF, namely, elemental analysis, PXRD, TGA, and DSC. The instructor should explain the experimental setup of all instruments to the students and guide them through the sample preparation procedures for PXRD, TGA, and DSC measurements (details are given in the [Supporting Information](#)). The PXRD pattern should be collected in the diffraction angle range 4–50° 2θ with a recommended step size of 0.02 over a total collection time of 20 min. Students are instructed to compare the respective experimental PXRD patterns with the calculated powder patterns generated using the freeware Mercury offered by the Cambridge Crystallographic Data Centre.²⁵ Thermal stability of the synthesized material is determined by TGA and DSC measurements, which are carried out in a dynamic inert atmosphere with a heating rate of 10 °C min⁻¹ from 25 to 300 °C. TGA provides insights into the temperature-dependent mass changes occurring in the sample and can be employed to determine the solvent content and activation conditions. The heat flow as a function of temperature is visualized by DSC measurements and provides useful insights into the nature of observed exothermic–endothermic transitions.

Stage three of the experiment requires students to activate the MOF, a process necessary to remove residual water and/or crystal lattice water from the pores. Activation is achieved by heating the MOF under oil-pump vacuum at 80 °C for 60 min followed by volumetric N₂ and CO₂ adsorption measurements at given temperatures. Gravimetric adsorption measurements are performed using a TG analyzer in a pure CO₂ atmosphere, followed by a binary CO₂/N₂ gas mixture (15% CO₂ in N₂). The following data collection strategy was found to provide the most reliable data and should be cycled three times: heat to 150 °C at 10 °C/min, hold for 10 min (activation), cool to 25 °C, and then hold until the mass has stabilized (adsorption). The volumetric adsorption measurements typically require at least a few hours and often run overnight. Depending on the instrumental setup, for the sake of time constraints, it might be favorable to have groups paired up or rotate through the different experiments as needed. Alternatively, the students can adapt the raw data provided in the [Supporting Information](#) if any equipment is unavailable.

HAZARDS

Copper(II) acetate and 1,3-di(4-pyridyl)propane are harmful and dangerous for the environment. In addition, although never encountered in our experiments, tetrazolates are potentially explosive and highly flammable and hence should be handled under the supervision of the instructor. The hydrothermal process is carried out by heating an aqueous mixture in a closed container. Since the elevated pressures inside the container may cause catastrophic failure of the container, standard personal safety equipment should be worn at all times, including safety glasses and gloves. The students are provided with access to the MSDS for all chemicals, and are asked questions on safety aspects of the experiment as part of their prelab work.

RESULTS

This lab was carried out over the course of three years at Clarkson University, with additional trial runs at Texas A&M University and Virginia Military Institute involving a total of approximately 60 students. The students integrated data from multiple instrumental techniques, were given exposure to a research-like setting, and learned the limits of conclusions that can be drawn from each analytical technique. The students were asked to either answer questions in a more traditional lab report, or to write a research-style analysis paper of their findings, citing relevant literature and preparing figures. The analysis papers included an introduction on carbon capture and MOF chemistry, experimental procedures, results, and interpretation of their results in a discussion and conclusion section. Both analysis styles yielded good results, with the paper writing option yielding more thoughtful questions and a better understanding of the topic areas by the students. Details on the results of the synthesis and characterization of **1** are given in the following section.

Synthesis

Synthesis of **1** proved to be straightforward in terms of reaction and workup, with yields reported between 95% to 100%. Please note that all starting materials are commercially available; however, recent modifications of this lab have shown that the tzc ligand precursor 1*H*-tetrazole-5-carboxylic acid ethyl ester sodium salt can be prepared by standard organic synthesis protocols,²⁶ thus, if desired, providing a great two day addition to the scope of this lab. Students are given a brief explanation

regarding the in situ formation of tzc due to the hydrolysis of NaEtzc (Figure 2). On the basis of the starting molar ratios of reactants and the CHN elemental analysis (C 33.63, N 23.30, and H 3.30), the overall composition of **1** can be assigned as $\{[\text{Cu}(\text{tzc})\text{dpp}]_{0.5}\cdot 1.5\text{H}_2\text{O}\}_n$. The amount of water content can be further confirmed by TGA.

Analysis of Phase Purity

PXRD yields a one-dimensional “fingerprint” of the material and is an important technique for students to learn in order to determine phase purities of their samples. With very high success rates, the students were able to synthesize a phase pure product; one example of their experimental powder patterns, compared with the calculated pattern, is shown in Figure 3.

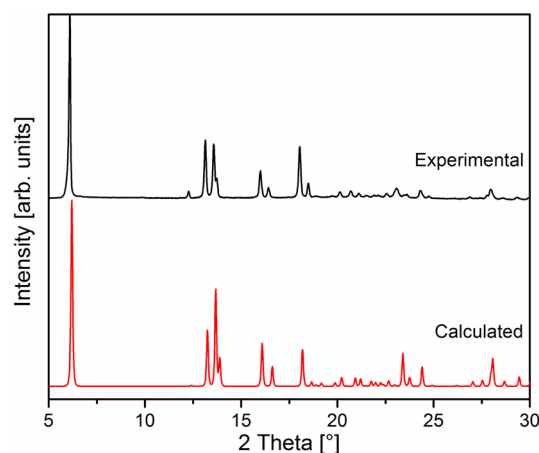


Figure 3. Experimental (top) and calculated (bottom) powder X-ray diffraction pattern of **1**.

During PXRD analysis, the instructor should emphasize the following: (i) the absence of additional reflections in the experimental pattern shows the existence of a pure crystalline phase, (ii) the slight shift of experimental reflection positions to lower 2θ diffraction angles is caused by the higher collection temperatures resulting in an expansion of the crystal lattice, (iii) due to preferred crystallographic orientations, referred to as texture effects, the experimental intensities may not match the calculated intensities.

Thermal Properties

TGA and DSC measurements are excellent tools for studying thermal behavior; additionally, they provide useful insights into the thermal stability of the material. Upon heating **1**, a two-step weight loss process can be observed (Figure 4). The first experimental weight loss of 8.9% is in very good agreement with that calculated for the release of the water molecules [$\Delta m_{\text{calc}}(1.5\text{H}_2\text{O}) = 9.0\%$], thus leading to the formation of the activated dehydrated phase $[\text{Cu}(\text{tzc})(\text{dpp})_{0.5}]_n$. The first step is accompanied by an endothermic event in the DSC curve at 81 °C, evidenced by the release of the water molecules, and step two is accompanied by an exothermic event at 218 °C according to the explosive decomposition of the tzc ligand. Please note that the absolute mass loss of the second heating step is imprecise due to the explosive nature of the decomposition of the tzc ligand, but it can be assumed that copper(II) oxide is formed as the final residue at higher temperatures. The tendency towards rehydration of the activated form by air moisture is emphasized by additional TGA analysis of the activated form after ambient air exposure.

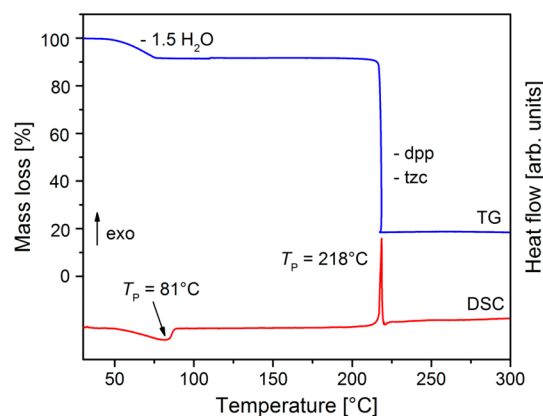


Figure 4. Thermogravimetric analysis (top) and differential scanning calorimetry curves (bottom) of **1**.

Adsorption Properties

Once the phase purity is confirmed and the students have gained knowledge regarding the thermal stability of the sample, adsorption measurements are performed. TGA provided detailed information on the activation conditions of **1**, revealing that the water removal process is completed in the temperature range 50–100 °C before decomposition at ~220 °C. An optimization of this process has shown that the material can be most economically activated at 80 °C under vacuum within 1–2 h.

CO₂ and N₂ adsorption isotherms of the activated material collected at various temperatures using standard protocols on a volumetric adsorption analyzer result in a preferred adsorption of CO₂ versus only negligible adsorption of N₂, emphasizing the potential of **1** to be used as carbon capture material (Figure 5A). It should be noted that the BET and Langmuir surface areas calculated from N₂ and Ar adsorption isotherms, collected at 77 and 87 K, respectively, do not accurately reflect the true internal surface area of **1** (Table 1). This can be attributed to diffusion limitations of N₂ and Ar, while CO₂ with its smaller kinetic diameter [$\sigma(\text{CO}_2) = 3.3 \text{ \AA}$ vs $\sigma(\text{N}_2) = 3.64 \text{ \AA}$ and $\sigma(\text{Ar}) = 3.4 \text{ \AA}$] can diffuse with no barrier into the 1-D channel nanopores of ~4 Å diameter, and thus, CO₂ is a more appropriate probe molecule for determining realistic specific surface areas in this case.

The CO₂ adsorption enthalpies were investigated to further quantify the carbon capture properties of **1**. This value can be calculated using two methods, namely by fitting experimental gas isotherms using both the virial and Langmuir equations in order to calculate zero-coverage heats of adsorption. The quantified values of ~40 kJ/mol fall well within the range of adsorption enthalpies considered to be ideal for CO₂ scrubbing from flue gas, which is additionally confirmed by binary gas adsorption measurements using a TGA analyzer (Figure 5B): mass gains of 5.0% and 2.9%, respectively, were observed by purging pure CO₂ and flue gas simulant (15% in N₂) over an activated sample of **1**.

SUMMARY

Students gained experience using a multitude of techniques, both by using the instruments themselves and by adapting the data supplied in the Supporting Information as “raw data” when equipment was unavailable. By making a compound that is easy to synthesize and has very clear properties due to its defined crystal structure and regular pore size distribution, the students

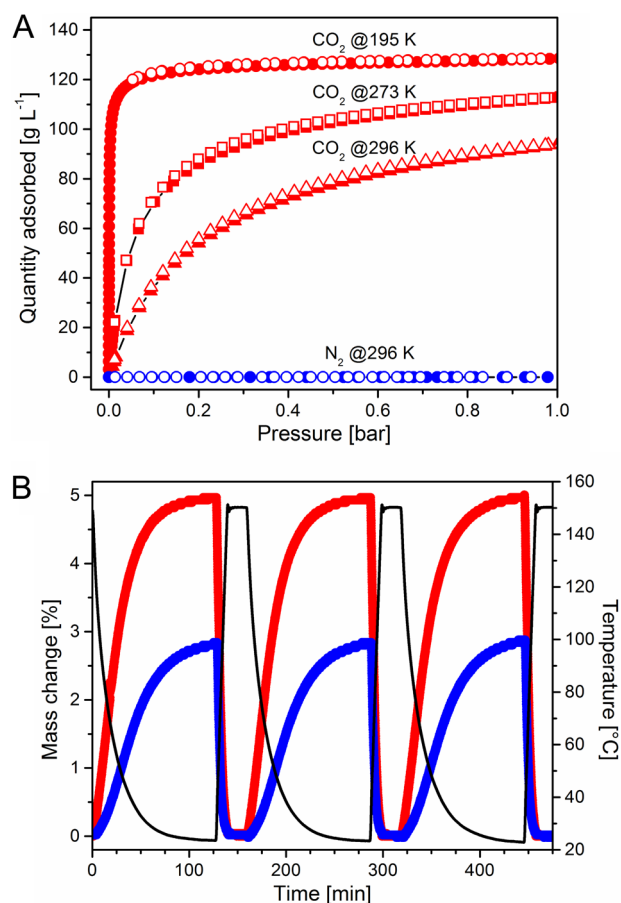


Figure 5. (A) Single gas adsorption isotherms of CO₂ (red) and N₂ (blue) (closed and open symbols represent adsorption and desorption, respectively). (B) Temperature-dependent gravimetric adsorption measurements with experimental mass changes shown as a function of temperature in pure CO₂ (red) and flue gas simulant (blue). The temperature is plotted as a black line.

Table 1. BET and Langmuir Specific Surface Areas Determined from Isotherms of Different Probe Molecules

Surface Area Measurements	N ₂ , 77 K	Ar, 87 K	CO ₂ , 195 K
BET, m ² /g	26.9	27.5	157.0
Langmuir, m ² /g	52.5	32.7	190.5

were able to clearly verify that they had successfully repeated a recipe. The mild noise in the data from each experimental device also provides a clear distinction between the raw data supplied and that collected from the experiment and can, in some calculations, lead to slightly different results, as is the case in real research laboratories. Students learned about the structure–properties relationship of a MOF and are now able to transfer these skills and characterization techniques to other porous materials that are used for carbon capture, gas storage (hydrogen, methane, etc.), or gas separation applications (e.g., oxygen/nitrogen). The rather in-depth section of calculations on gas adsorption and powder X-ray data, in particular, required the students to think critically about equilibrium, the physisorption process, various gas and kinetics laws, scattering behavior, and signal-to-noise ratios. We believe writing the research-style analysis paper yielded significant pedagogical value, as it prompted students to think more independently and

to verify their results and draw conclusions using experimental evidence supported by literature.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00258.

Student handout with detailed experimental instructions for the synthesis and experiments, and details for instructors (PDF, DOCX)

Sample raw data from powder X-ray diffraction, TG-DSC, and gas sorption measurements (XLSX)

Data and calculations for isotherms (XLSX)

Crystallographic structural information (CIF)

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Notes

The authors declare no competing financial interest.

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