Facilitating Laboratory Research Experience Using Reticular Chemistry

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S Supporting Information

ABSTRACT: Rapid development in the field of reticular chemistry has allowed scientists ever-increasing control over the design and synthesis of crystalline porous materials. The promise that this field has in the development of next-generation materials for numerous applications (gas storage and separation, catalysis, chemical sensing, electronics) relies on the effective training of new scientists in the diverse array of computational, synthetic, and analytical techniques that reticular chemistry requires. Herein, we describe a laboratory-research experience designed to equip a class of upper-division undergraduates in chemistry and chemical engineering not only with these skills but also the skills necessary to communicate their future research accomplishments to the greater scientific community. The course is subdivided into three modules: (i) synthesis, characterization, and post-synthetic modification of metal−organic frameworks; (ii) superacid catalysis with metal−organic frameworks; and (iii) synthesis, characterization, and gas adsorption applications of covalent organic frameworks.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Inorganic Chemistry, Organic Chemistry, Physical Chemistry, Computational Chemistry, Communication/Writing, Acids/Bases, Crystals/Crystallography*

Reticular Chemistry
Synthesis, Characterization, Properties, and Communication

MOF-5   COF-5   MOF-808
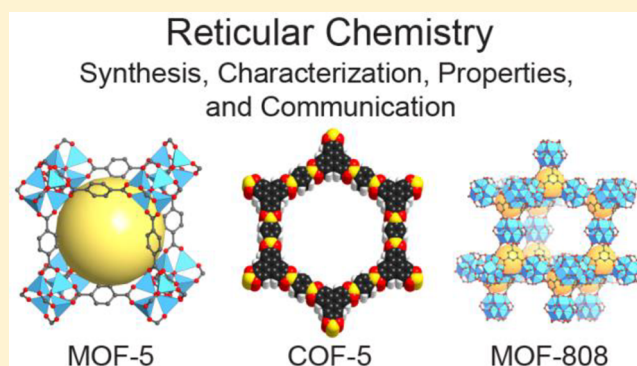
INTRODUCTION

Metal−organic frameworks (MOFs) and covalent organic frameworks (COFs) have emerged over the past two decades as classes of designable, porous, crystalline materials with exceptional structural diversity and tunable chemical functionality.[1,2] These materials are formed from polyfunctional, geometrically predefined organic compounds, commonly known as linkers, connected through coordination to metal clusters (known as secondary building units, or SBUs) in MOFs and through reversible organic linkages (most often from condensation reactions) in COFs. Through judicious choice of organic linking groups and an understanding of the underlying linkage chemistry, the structure of a MOF or COF upon reticulation of its subunits can often be predetermined.[3] This detail is the clearest dividing line between traditional solid-state material discovery and the still burgeoning field of reticular chemistry. In the former, synthesis is often haphazard and driven by chance. Without synthetic predictability, the identification of structure−property relationships is only as useful as the ability to successfully prepare a new material with the desired structural features. In reticular chemistry, however, overall structure and chemical functionality are a product of design, allowing for direct application of our understanding of the current generation of porous materials to the design of the next.

In bridging between a number of chemical disciplines (organic, inorganic, and physical), reticular chemistry provides a unique opportunity as a teaching tool. Students are exposed to a series of traditional subdisciplines in undergraduate chemistry curricula but do not have sufficient opportunities to combine and apply the concepts they learn to materials science and real-world applications. Indeed, MOFs and COFs have been investigated as materials for gas storage and separations,[4,5] catalysis,[6,7] sensing,[8,9] and electronics,[10,11] among other applications.

Despite their prominence in the chemical literature, they remain largely absent from laboratory courses found in undergraduate chemistry programs. Even in the chemical-education literature, few publications on reticular chemistry exist.[12−16] In an effort to remedy these deficits, we developed and taught a three-module laboratory and lecture course covering fundamental concepts, synthetic techniques, and characterization methods used in the field of reticular chemistry. The class was composed of 28 upper-division undergraduate students, coming from various locales around the world and studying chemistry, chemical engineering, and materials science. The final week of the program focused

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entirely on science communication, culminating in a poster session in which students presented their work on one of the preceding weeks' modules, as well as a paper writing and review exercise in the format of an American Chemical Society journal communication.

■ MODULE 1: SYNTHESIS, CHARACTERIZATION, AND POST-SYNTHETIC MODIFICATION OF MOFS

The first laboratory module of this program was adapted and modified from a previous publication in this journal by our colleague John Arnold.[12] (The Supporting Information for Module 1, including example data and procedures, can be found in ref 12). We chose this experiment as it serves to introduce general concepts, synthetic techniques, and characterization methods essential to the understanding of reticular materials. The design of a new MOF begins first with a choice of organic linker, often a polycarboxylic acid, and metal salt. These reagents are then dissolved as completely as possible in a solvent or solvent mixture, typically an amide solvent such as dimethylformamide. The solvothermal synthesis then proceeds for 12 h to 7 days or more. The identity of the linker and metal salt and the chosen solvent, temperature, and reagent concentration are all parameters that must be varied by the experimenter to determine optimal crystallization conditions. Often, numerous attempts are necessary in order to crystallize a new MOF.

In this experiment, the students were exposed to characterization techniques that are often only encountered in a scientific research setting. These include powder X-ray diffraction (PXRD), thermal gravimetric analysis (TGA), and gas adsorption isotherms interpreted using Brunauer–Emmett–Teller (BET) theory. We also introduced the concept that synthetic manipulations of MOFs and COFs do not necessarily end after crystallization. Solid-state organic and organic–inorganic hybrid materials possess much of the same reactivity their molecular counterparts do in solution. post-synthetic modification as a means of performing chemistry on a framework allows the covalent attachment of functional groups to the structure that may not be compatible with the crystallization conditions. Specifically, this module focused on the synthesis and characterization of MOF-5 and IRMOF-3 (Figure 1). The latter of these is subjected to a post-synthetic-modification procedure and further characterized through digested nuclear magnetic resonance (NMR) experiments.[12]

MOF-5 and IRMOF-3 are both formed through the linkage of 1,4-benzenedicarboxylate units through octahedral $[Zn_4O]^{6+}$ clusters. These linear and octahedral building blocks combine to form primitive-cubic lattices, with the only difference between them being that IRMOF-3 contains a single amino group on each of its carboxylate linkers (Figure 1). This allows for the introduction and exploration of the isoreticular concept. Isoreticular frameworks are those that possess the same underlying structure, in this case a primitive cubic lattice, but have unique pore metrics and functionality.

Students prepared MOF-5 solvothermally by heating solutions of 1,4-benzenedicarboxylic acid and zinc nitrate hexahydrate in dimethylformamide (DMF) at 80 °C for 10 h. Likewise, IRMOF-3 was prepared by heating solutions of 2-amino-1,4-benzenedicarboxylic acid and zinc nitrate hexahydrate in DMF at 100 °C for 18 h. Each of these materials was subjected to solvent exchange sequentially with DMF and dichloromethane (DCM) to remove excess metal salts and
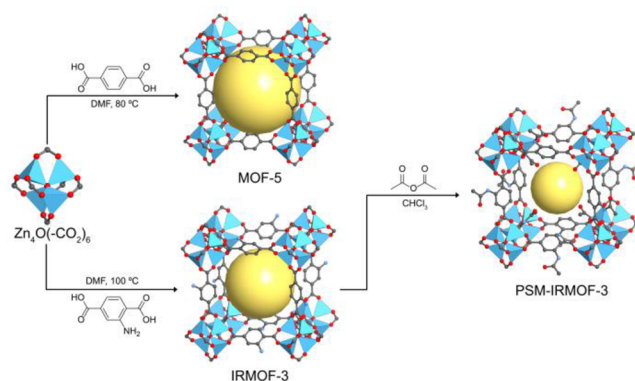

Figure 1. Synthesis of MOF-5 and IRMOF-3 and post-synthetic introduction of amide groups onto IRMOF-3 yielding PSM-IRMOF-3. In the diagram of the SBU on the left, the $-CO_2$ units originate from the carboxylate linkers and have been truncated to highlight the structure and coordination geometry of the cluster. Yellow spheres represent the frameworks' free spaces and have no chemical meaning. Atom colors: Zn, blue tetrahedra; C, gray; O, red; and N, blue. H atoms are omitted for clarity.

linker from their pores, and the remaining DCM was removed from the materials *in vacuo* prior to initial characterization. This process is often referred to as activation.

After completing the synthesis and solvent exchange of MOF-5 and IRMOF-3, students confirmed the crystallinity of their materials through measurement of their PXRD patterns between 2θ angles of 5 and 40°. These patterns were compared visually to those in the published literature (Figure 2a). In practice, PXRD measurement of framework materials is unique because of the following considerations: (i) Peaks or reflections in a PXRD pattern correspond to groups of planes within a structure containing identical spacing. In framework materials, these often include reflections with 2θ angles <10°, indicative of their large unit cells. (ii) Verification of a structure comes first from a full matching of all Bragg reflection positions, with relative intensity as a secondary consideration. (iii) Low angle reflections tend to be the most intense because framework materials often have a greater degree of order at longer length scales. (iv) Finally, in contrast to other crystalline materials, framework materials can often be measured while wet with solvent. This can have consequences in the interpretation of the resulting PXRD pattern.

Students then performed TGA measurements on their MOF-5 and IRMOF-3 samples, heating them under air flow from 25 to 650 °C. There are two primary mass losses during this experiment: removal of residual solvents from the material and combustion and removal of the carboxylate linkers (Figure 2b). The remaining mass in the material after the experiment can be attributed solely to zinc oxide. This, along with the mass loss due to removal through combustion of the carboxylate linkers, was used by students to determine the molar ratio of linker to zinc, further corroborating the chemical composition of their materials.

Most MOFs display surface areas significantly higher than those of other porous materials such as zeolites and porous carbons. This has spurred intense investigation of these materials as sorbents for industrial applications, such as hydrogen and natural gas storage in automobile applications, CO_2 capture, gas separation, and catalysis.[17−19] In addition to PXRD and TGA experiments, students also collected N_2 isotherms of their activated MOF-5 and IRMOF-3 samples
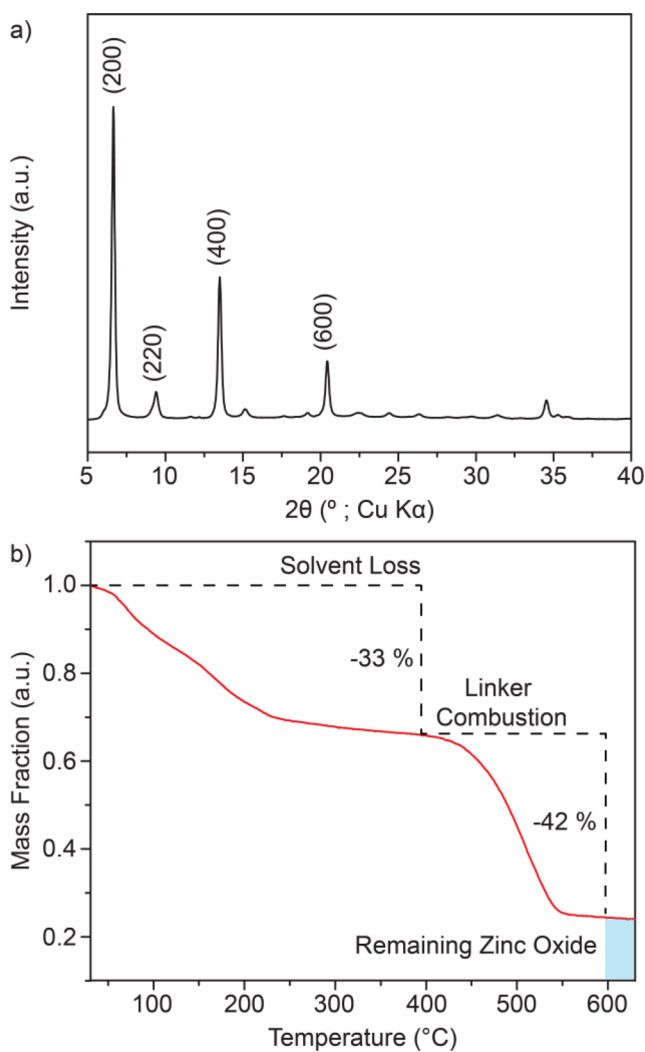
Figure 2. (a) Representative PXRD pattern of MOF-5 with Miller indices of the most intense reflections identified and (b) TGA data (under air flow) for MOF-5 showing solvent loss, linker combustion, and metal oxide residue.

with a low-pressure adsorption analyzer. Using the instrument's analysis software, students determined the surface areas of their samples using BET theory.[12] After completing the aforementioned characterization of their synthesized MOFs, students post-synthetically modified the amine group on IRMOF-3 to an amide group through exposure of the material to a solution of acetic anhydride in chloroform. Though direct synthesis of the resulting amide containing MOF is likely possible, this reaction serves as an accessible example of how MOF linkers can be post-synthetically modified without fundamental alteration of the MOF lattice. In order to determine the degree of conversion of their post-synthetic modifications, students decomposed samples of treated MOF in mixtures of concentrated DCl in D_2O and DMSO-d_6. The resulting solutions of linker and metal salts were analyzed by liquid-state ^1H NMR spectroscopy, allowing students to determine the ratio of amine and amide linker in their post-synthetically modified MOF.[12]

In summary, this module's experiments exposed the students to many of the fundamental aspects of reticular chemistry. Students learned: (i) general principles behind the reticulation of geometric subunits into extended networks; (ii) synthetic

considerations in the solvothermal synthesis of MOFs; (iii) collection and interpretation of MOF PXRD patterns; (iv) use of TGA to determine and corroborate a MOF's molecular formula; and (v) methods and spectroscopic techniques for completion and analysis, respectively, of post-synthetic modifications of MOFs.

■ MODULE 2: SUPERACID CATALYSIS WITH MOF-808

To demonstrate the breadth of applications available to MOFs and reticular materials in general, we sought to expose the students to a recently published experiment utilizing MOFs for catalytic applications.[20] Toward this end, microcrystalline MOF-808 $(Zr_6O_4(OH)_4(BTC)_2(HCOO)_6$, BTC^{3-} = 1,3,5-benzenetricarboxylate) and its acidified counterparts (MOF-808−xSO_4; x = 0.65, 1.35, or 2.5) were selected as the materials of choice for the second module. In MOF-808, the inorganic SBUs are composed of six zirconium atoms linked together by BTC^{3-} (each BTC^{3-} is connected to three SBUs) to form the extended framework. To balance the charge, yielding a neutral framework, the coordination sphere of each zirconium atom in the SBU is completed with six formate ligands. It has been previously reported that these relatively reactive formate ligands can be replaced with sulfate ligands, leading to superacidity in MOF-808−xSO_4 materials.[20]

Superacids are defined as compounds with Hammett acidity functions ≤ -12. Because of the leveling effect and the fact that superacids are more acidic than the hydronium ion, their strength in water is difficult or impossible to measure. For this reason, a new acidity scale, Hammett acidity, was devised.[21] Typically, Hammett acidity is measured using a series of progressively weaker bases, often substituted anilines. These compounds undergo a color change dictated by the protonation state of the aromatic amine. For this reason, UV−vis spectroscopy can be utilized to determine if a given acid is stronger than the conjugate acid of the indicator molecule. More simply, these color changes can be so distinct that the naked eye can often detect them, which leads to simple experimentation to confirm the superacidity of compounds such as the MOF-808 samples examined in this experiment.

A variety of have been superacids reported, and they have been used in numerous applications, such as heterogeneous catalysis and hydrocarbon activation.[21] In fact, superacids were instrumental in the work leading to the 1994 Nobel Prize in Chemistry, awarded to the late George Olah for his contribution to carbocation chemistry.[22] Examples of liquid superacids (e.g. HF−SbF_5, HSO_3F, and CF_3SO_3H) are relatively common, but in many cases, they remain difficult to handle and pose environmental threats. For this reason, focus has been placed on the development of solid superacids such as sulfated zirconia, Nafion-H and zeolite HY.[23−29] Recent work from our group detailed superacidification of MOF-808 with the goal of creating a structurally and chemically well-defined solid-state superacid, with emphasis on precise determination of the level of acidity and knowledge of the nature of the acidic sites.[21]

Samples of MOF-808 were pre-synthesized for the students and activated to remove extra reactants and solvent from the pores. This procedure was necessary because there was limited time for the students to complete the two-week procedure of synthesizing and washing the MOFs. Additionally, students had already been exposed to the process of solvothermal
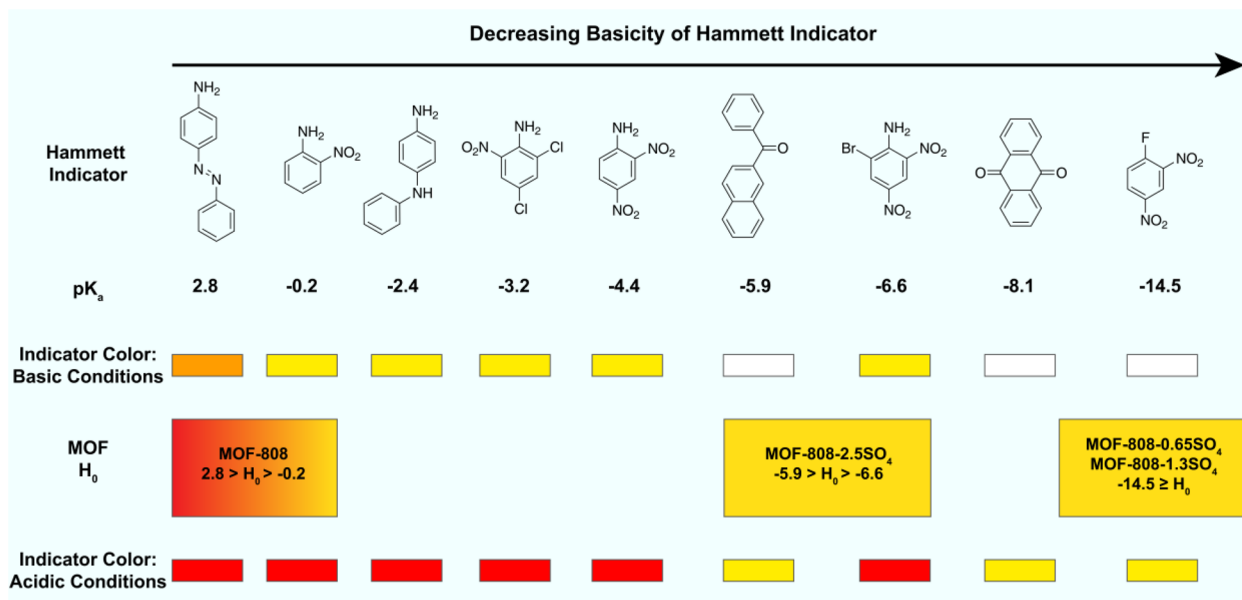
Figure 3. Hammett-indicator results for sulfated (MOF-808−0.65SO$_4$, MOF-808−1.3SO$_4$, and MOF-808−2.5SO$_4$) and nonsulfated MOF-808 samples. Entries in the row "MOF H_0" detail the approximate color of the indicator solution when exposed to that MOF sample. H_0 is defined as the Hammett acidity value of that material. MOF-808 produced a color change in the first Hammett indicator solution (4-phenylazoaniline) but not in the second Hammett indicator solution (2-nitroaniline), thereby indicating that its H_0 value is between the pK_a values of those indicators. Similar interpretation was carried out for the sulfated samples.

synthesis and MOF washing and activation during the first module. Therefore, the students received presynthesized MOF-808 samples and began the process of exchanging the formate ligands for sulfates by immersing the samples in aqueous solutions of H$_2$SO$_4$ of various concentrations. These samples were used for demonstration of the process of sulfation only and were discarded. The students were then given samples of pre-prepared MOF-808−xSO$_4$. Conventional PXRD and FT-IR analysis were performed on all MOF-808−xSO$_4$ samples (see the Supporting Information (SI), Module 2, teacher manual). The students then performed Hammett indicator tests on the four MOF-808−xSO$_4$ samples by adding sample MOF-808−xSO$_4$ to nine separate indicator solutions (Figure 3). Students then used the pK_a values for the Hammett indicators to determine a range of Hammett acidity values for the solid samples.

As a demonstration of the catalytic activity of the MOF-808−xSO$_4$ samples, students conducted two representative acid-catalyzed reactions, namely the cyclization of (±)-citronellal (Table 1) and isomerization of α-pinene (Table 2). To characterize the yields and product distributions (as a measure of selectivity) of the two reactions, students utilized a gas-chromatography mass-spectrometry instrument equipped with a SHRXI-5MS capillary column. In order to determine yields for each reaction, the combined groups of students determined calibration curves for (±)-citronellal and α-pinene, as well as the expected products for each acid-catalyzed reaction. To conclude this experiment, students analyzed the Hammett acidities of the various MOF-808−xSO$_4$ samples, compared and contrasted these results with the PXRD and FT-IR data collected, and used this information to corroborate the analysis of the catalytic reactions.

In summary, this module allowed the students to explore some of the most powerful concepts of reticular chemistry with applications to post-synthetic modification and catalysis. Students learned: (i) post-synthetic modification techniques

Table 1. Conversion and Yield for the Cyclization of (±)-Citronellal Using MOF-808 at Various Degrees of Sulfation[a]
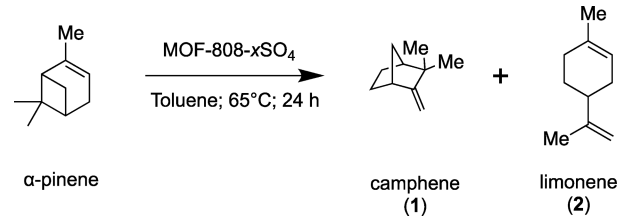

Entry	Catalyst	Conversion (%)[b]	Yield (%)[b]
1	MOF-808	72	72
2	MOF-808−0.65SO$_4$	65	65
3	MOF-808−1.3SO$_4$	100	100
4	MOF-808−2.5SO$_4$	100	100

[a]Reaction conditions: 0.83 mmol of (±)-citronellal, 5.0 mg of catalyst, 1 mL of toluene, inert (N$_2$) atmosphere, 65 °C, 24 h. [b]Yields and conversions were calculated from GC-MS analysis.

to install acidic sulfate groups in framework materials; (ii) general concepts associated with acidity and superacidity as well as means of probing those properties; (iii) methods associated with conducing catalytic reactions; and (iv) analytical techniques associated with elucidating parameters (yields and conversions) of catalytic reactions, including the use of calibration curves and internal standards. Full student and teacher manuals can be found in the SI (Module 2, student and teacher manuals).

■ MODULE 3: SYNTHESIS, CHARACTERIZATION, AND GAS ADSORPTION PROPERTIES OF COFS

COFs, like MOFs, are porous crystalline solids formed from the reticulation of geometrically predefined linking groups; however, they possess several key differences. COFs are composed entirely of light elements (e.g. C, H, B, O, Si, and

Table 2. Conversion and Yield for the Isomerization of α-Pinene Using MOF-808 at Various Degrees of Sulfation[a]

Entry	Catalyst	Conversion (%)[b]	Yield 1 (%)[b]	Yield 2 (%)[b]
1	MOF-808	21	0	3
2	MOF-808−0.65SO$_4$	94	13	3
3	MOF-808−1.3SO$_4$	56	27	9
4	MOF-808−2.5SO$_4$	—	35	17

[a]Reaction conditions: 2 mmol of α-pinene, 10.0 mg of catalyst, inert (N$_2$) atmosphere, 120 °C, 48 h. [b]Yields and conversions were calculated from GC-MS analysis.

N) and are linked entirely through covalent bonding.[30] Unlike MOFs, COFs are almost always linked through single connection points, leaving predefined organic units as the only vertices within the structure. In MOFs, the geometry of the SBU formed in a reaction is sometimes difficult to predict, leaving a larger amount of uncertainty in structural prediction. This difference drastically reduces the number of likely structures for a COF relative to that for a MOF given a particular set of linker geometries. Another key difference is in how COFs are characterized. Often, MOFs can be characterized through single-crystal X-ray diffraction. In contrast, COFs are nearly always obtained as polycrystalline powders whose PXRD patterns contain only a handful of reflections, making structural solution by direct methods impossible. For this reason, COF characterization often begins with the creation of a structural model using a software suite, such as Materials Studio.[31] This model is then Pawley refined against the experimental powder-diffraction pattern to obtain the unit-cell information.[32] In combination with FT-IR spectroscopy of the sample to confirm formation of the covalent linkage and a pore-size distribution determined from its N$_2$ isotherm, these data provide strong supporting evidence for the formation of a particular structure. As an illustration of these concepts and characterization processes, Module 3 focused on the synthesis of COF-5, an eclipsed hexagonal COF formed through boronate ester linkages (Figure 4). For this laboratory module, COF-5 was produced using rapid-synthesis techniques and characterized in the aforementioned manner.[33−35]

COF-5 is formed from the condensation of hexahydroxytriphenylene (HHTP) and 1,4-benzenediboronic acid (BDBA). The formation of boronate ester linkages between these trigonal and linear linkers results in the formation of an extended hexagonal lattice, which stacks in an eclipsed fashion resulting in a series of one-dimensional channels along the stacking direction.[33,34] During this week, students were also introduced to the concept of isosteric heat of adsorption (Q_{st}). In developing porous materials for gas separation or storage, it is important to know the adsorbent−adsorbate affinity associated with the physisorption of a particular gas onto the surface of a material. Students performed CO$_2$ isotherms on their COF-5 samples at two different temperatures and determined the Q_{st} of CO$_2$ using the Clausius−Clapeyron equation.[36]

Prior to synthesizing COF-5, students were taught to build and optimize models of its structure in Materials Studio and then simulate PXRD patterns from the obtained structure (SI, Module 3, teacher manual). This modeling exercise provided students with an opportunity to visualize the relationship between a structure and its PXRD pattern. In particular, students used Bragg's Law to relate the 2θ angles of the (100) and (001) reflections to the pore size and interlayer spacing distance of their COF structure.

After successfully modeling their expected structure, students synthesized COF-5 solvothermally from a suspension of HHTP and BDBA in a mixture of mesitylene and 1,4-
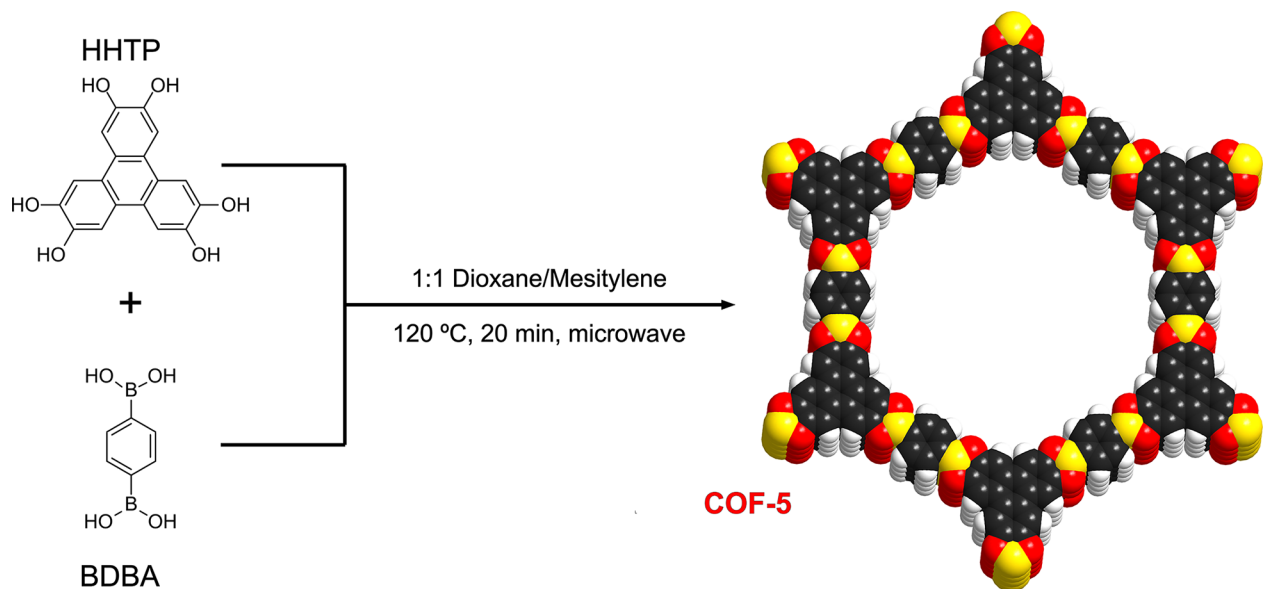

Figure 4. Synthesis of COF-5 by boronate ester condensation between hexahydroxytriphenylene (HHTP) and 1,4-benzenediboronic acid (BDBA). Atom colors: C, black; B, yellow; O, red; and H, white.

dioxane in a microwave reactor at 100 °C for 30 min. The resulting solids were solvent exchanged twice with anhydrous acetone in the microwave reactor for 20 min and then dried *in vacuo*. A wide variety of linkage reactions and synthetic conditions are used in the synthesis of COFs, but in all cases, dynamic reversibility of the linkage is a key feature. No crystallization process is error-free, and linkage reversibility ensures that individual linkage sites that do not correspond to the thermodynamically most stable COF phase have the opportunity to break apart and reform "correctly".[34]

Once students obtained dry samples of COF-5, they collected PXRD patterns of each between 2θ angles of 2 and 35° (where reflections are observable for this material) and performed a Pawley fitting between their experimental data and model using Materials Studio's Reflex module (Figure 5a;
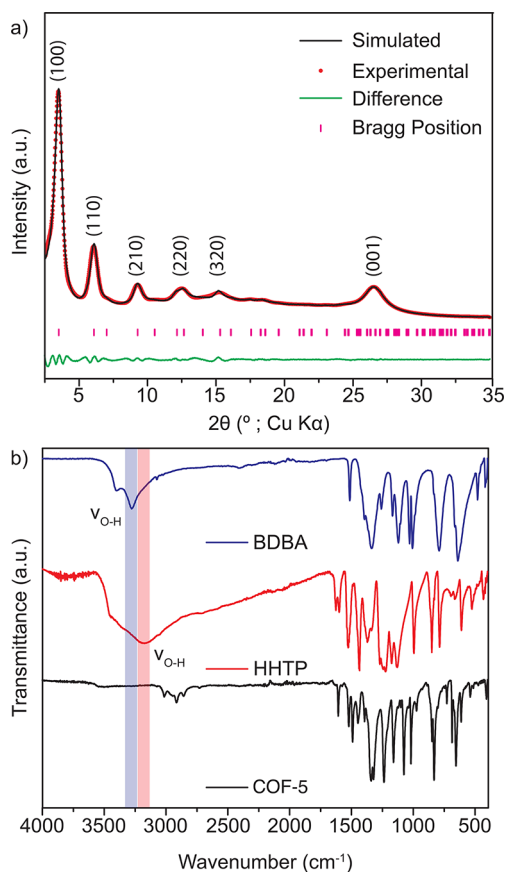

Figure 5. (a) PXRD pattern of activated COF-5 with a Pawley refinement showing the experimental pattern (red dots), the simulated pattern from a computational model (black line), the difference (green line), and the Bragg positions (pink bars). (b) FT-IR comparison between COF-5 (black) and the starting materials HHTP (red) and BDBA (blue) showing the disappearance of $\nu_{O\text{-}H}$ stretching frequencies.

SI, Module 3, teacher manual).[31] Students also collected FT-IR spectra of their COF samples, from which they could observe the formation of their respective linkages. For COF-5, students observed the disappearance of catechol and boronic acid O–H stretching frequencies in the FT-IR of their activated COF-5 samples (Figure 5b; SI, Module 3, teacher manual).[37]

Samples of activated COF-5 were also analyzed by N_2 and CO_2 adsorption isotherms, with the latter being measured at both 298 and 273 K (SI, Module 3, teacher manual). In a

manner identical to that in Module 1, students calculated the surface area and pore-size distribution of their COF-5 samples from their N_2 isotherm data. The obtained pore sizes were then compared and shown to be in agreement with those measured from the model structure. Using the Clausius–Clapeyron equation, students calculated the isosteric heat of adsorption of CO_2 in COF-5 from their CO_2 isotherms (SI, Module 3, teacher manual).[36] For the sake of simplicity, students were instructed to approximate their isotherms as linear functions. This method results in a single approximate value for Q_{st} rather than one that varies with uptake. Nonetheless, this provided the students with a basic understanding of the calculation and an example of how a thermodynamic parameter can be extracted from isotherm data.

In summary, this module exposed students to some of the unique synthetic and analytical techniques used in the study of COFs, and it provided an introduction to more advanced gas adsorption experiments and the accompanying calculations. Students learned: (i) Computational chemistry by using of Materials Studio's software modules to simulate COF structures, their PXRD patterns, and their surface areas, as well as by performing Pawley refinement in order to compare experimental PXRD patterns to that of the model; (ii) Synthetic considerations specific to the synthesis of COFs using condensation reactions, with an understanding of dynamic error correction in the process of crystallization; and (iii) How to calculate the isosteric heat of adsorption of a gas to a framework using gas adsorption isotherms. Full student and teacher manuals can be found in the SI (Module 3, student and teacher manuals).

■ SCIENTIFIC COMMUNICATION: MANUSCRIPT PREPARATION AND POSTER PRESENTATION

After completion of these three laboratory modules, students undertook a poster making and publication drafting exercise using a laboratory module of their choice, which was designed to familiarize them with methods of communication found in the larger scientific community. During the laboratory modules, students were instructed in the use of OriginPro (data analysis and graphing), Diamond (crystal structure visualization), and Adobe Illustrator as tools to convert the data they collected during their laboratory experiments into publication quality figures.[38−40] In designing figures, students were required to carefully consider what ideas and information they intended to communicate to the audience.[41−43] We consider the design of figures to be an integral part of refining the ideas behind a scientific work and condensing it into a form that both clearly communicates the intent and result of the work and holds the reader's attention through its visual appeal. Figures in hand, students set upon designing posters for a poster competition, where their work was presented to the UC Berkeley College of Chemistry and was judged by a panel of graduate students.

Aided by a paper writing workshop, students also prepared a manuscript in the format of a *Journal of the American Chemical Society* communication using the results of their chosen module.[44−49] After completion of their manuscripts, students submitted them via email to an "editor" who then forwarded them to the module instructors for review. Reviews were written to resemble as closely as possible what one might receive from a real submission to a journal, along with recommendations to reject, accept with major revisions, accept

with minor revisions, or accept as is. It was our objective that this simulation would provide students with the skills necessary to effectively communicate their future research to the greater scientific community and achieve the publications necessary for a successful scientific career. Indeed, our objective was accomplished in that three of our students' work was published shortly after the completion of the program.[50]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b00265.

Student manual for Module 2 (PDF, DOCX)
Teacher manual for Module 2 (PDF, DOCX)
Student manual for Module 3 (PDF, DOCX)
Teacher manual for Module 3 (PDF, DOCX)
COF-5 structure (CIF)

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Notes

Software instructions including screenshots for Materials Studio found in the ᔆᵘᵖᵖᵒʳᵗⁱⁿᵍ ᴵⁿᶠᵒʳᵐᵃᵗⁱᵒⁿ were generated using software programs from Accelrys Software Inc. Specifically, Materials Studio's Forcite module was used to simulate and perform geometry optimizations on COF-5. Materials Studio's Reflex module was used to simulate PXRD patterns and perform Pawley refinements for COF-5. This software and the corresponding screenshots were all used with permission from Accelrys Software Inc. in accordance with their guidelines. Likewise, software instructions including screenshots for Quantachrome software were used with permission from Quantachrome Instruments.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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