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Inorganic Chemistry Laboratory Experiment on the Zeolitic Imidazolate Framework ZIF-8, a Typical Example of Metal Organic Framework

Umit B. Demirci*, Laurent Bernaud

Departement de Chimie, Faculte des Sciences, Universite de Montpellier, 34090, Montpellier, France
*Corresponding author: umit.demirci@umontpellier.fr

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Abstract Because our undergraduate chemistry students hear about metal organic frameworks (MOF) within the plan of the teaching units dedicated to inorganic chemistry and coordination chemistry, we initiated in 2017-2018 an inorganic chemistry laboratory experiment aimed at third-year undergraduate students (7 sessions of 4 h each). The laboratory focuses on the synthesis and analysis of the ZIF-8, a well-documented and easy-to-synthesize MOF. Students are introduced to coordination chemistry, MOFs, solvothermal synthesis, analysis techniques (scanning electron microscopy, X-ray diffraction, Fourier transform infra-red spectroscopy, thermogravimetric analysis), and 3D visualization of the structural models of crystalline solids. Prior to any discussion with the instructor, the students are strongly encouraged to analyze their collected data based on the open literature, and it is expected that they will develop their autonomy. The students gain experimental independency. After the laboratory experiment, the students prepare a poster (2 dedicated sessions, of 4 h each), and present it during an oral examination (10^{th} session) in front of a jury of four instructors. In this way, they are assessed. We believe that this inorganic chemistry laboratory experiment could be adopted by other laboratories as it is, or in an adapted form. Some suggestions to adapt it are made.

Keywords: *inorganic chemistry, Coordination chemistry, MOFs, Solvothermal synthesis, ZIF-8*

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1. Introduction

Rapidly growing metal organic frameworks (MOF) belong to an important class of porous materials [1,2]. They consist of metal nodes (ions or clusters) that are coordinated to organic ligands (linkers). A typical example is the MOF called ZIF-8, with ZIF for zeolitic imidazolate frameworks [3]. In this MOF, the Zn^{2+} is tetrahedrally coordinated to 2-methylimidazole $CH_3C_3H_2N_2H$ ligands through the N atoms (Figure 1). The importance of MOFs can be illustrated as follows: in 2020, over 90,000 synthesized MOFs have been inventoried, and over 500,000 MOFs have been predicted; furthermore, there is a potential of millions of distinct MOFs owing to the higher number of possible metal nodes and organic ligands that could be coordinated [4].

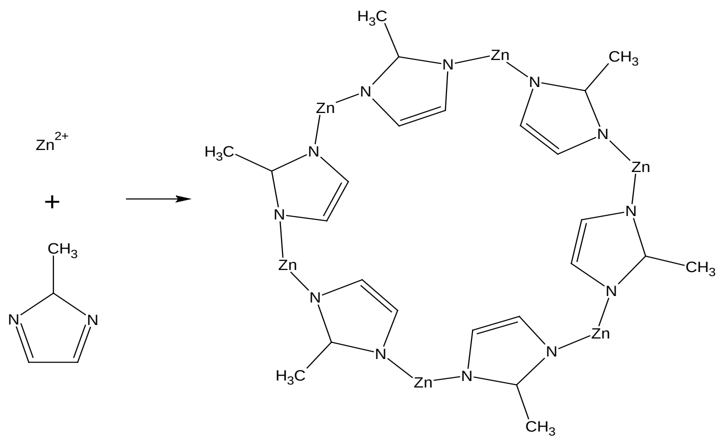

Figure 1. ZIF-8 where Zn^{2+} is coordinated to 2-methylimidazole ligands through N atoms

MOFs have a dominant position in research and, by extension, in university education [5-9]. MOFs are indeed cited as typical illustration examples in various teaching units on chemistry (e.g. solid state, porous materials, coordination compounds, polymers). They are also key examples to illustrate applications in the fields of energy and environment, with applications such as CO_2 capture and separation. This is the case of our department of chemistry, where the undergraduate chemistry students hear about MOFs early on in their curriculum.

In this context, we developed an inorganic chemistry laboratory experiment aimed at third-year undergraduate chemistry students, focusing on the synthesis and analysis of a well-documented MOF. We chose to work on ZIF-8 because it can be synthesized by an easy and safe method [10] that is accessible to undergraduate chemistry students. We started the inorganic chemistry laboratory experiment in the academic year 2017-2018, and twelve third-year undergraduate chemistry students have successfully experimented it over the last academic years (see supporting information (SI)). Through the experiment, the students are introduced to coordination chemistry, to MOFs through a representative example (ZIF-8), to the solvothermal synthesis method, and to advanced analysis techniques (scanning electron microscopy, powder X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, for example). Accordingly, they gain hands-on experience in the mentioned techniques, as well as in 3D visualization of structural models of crystalline solids. They also have an overview of what is the academic research, especially through tasks related to bibliographic search, experimentation, data analysis and discussion, and the preparation of a poster. Upon completion of the experiment (10 laboratory sessions, where 7 are dedicated for the syntheses and analyses, and 2 for the poster preparation; see SI for details), the students are assessed by a jury composed of four instructors (during the 10th laboratory session). Typically, they present the poster of the work done and the jury asks questions, having a discussion with the students.

2. Materials and Methods

2.1. Safety and Hazards

The inorganic chemistry laboratory experiment on the ZIF-8 is accessible to undergraduate chemistry students. The usual safety precautions must be taken. The students must wear a labcoat, and safety glasses. They must use protective gloves. They must work under a fume hood. In addition, they must dispose of any waste, reactant, solvent, product and by-product in the dedicated waste containers.

2.2. Experimental Procedure

ZIF-8 can be synthesized by different methods [10] but we chose to use the solvothermal one because it is easy to set up. We firstly considered two different solvents, *N,N'*-dimethylformamide (DMF) and methanol CH_3OH, but we soon focused on the DMF solvent owing to higher yields (~40% at each attempt versus <20%) and excellent reproducibility. ZIF-8 is synthesized as follows, knowing that we repeat the protocol reported in the reference mentioned above. Typically, 670 mg of zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ (98%, from Analytic Lab; 297.5 g mol^{-1}), 187 mg of 2-methylimidazole $CH_3C_3H_2N_2H$ (97%, from Analytic Lab; 82.1 g mol^{-1}), and 50 mL of DMF (99%, from Analytic Lab) are mixed together, and the mixture is stirred to obtain a clear solution. The solution is transferred into a Teflon lined stainless steel autoclave (100 mL) and heated at 140°C in an oven. The heating is stopped after 24 h (by the laboratory technician in our context), and students works on it the week after (in our context, there are weekly sessions of 4 h each). The ZIF-8 powder is filtered, washed with DMF three times, washed with methanol (99.8% from Analytic Lab) three times, and then dried in an oven at 60°C. The synthesis is repeated twice or thrice for the sake of reproducibility (see SI, on page 5 for details about the work plan), and for collecting enough ZIF-8 for the following analyses.

In our laboratory, the students have fair access to analysis techniques (see SI) such as scanning electron microscopy (SEM; JEOL JSM-6010PLUS/LA), X-ray diffraction (XRD; Philipps goniometer and Seifert generator), Fourier transform infra-red (FTIR) spectroscopy (Perkin Elmer Frontier, with ATR pike GladiATR), and thermogravimetric (TG) analysis (Perkin Elmer STA 6000). The students are trained on the techniques, so they can prepare and analyze their samples on their own (with the support of the laboratory technician and/or the instructors).

2.3. Scheduling of the Laboratory Sessions

This laboratory experiment requires, in our conditions and depending on the potential of students (who are expected to work in partial autonomy), 6 to 7 sessions of 4 h each. In the 1st session, the students prepare the chemicals and the material, and they work on the calculations for a first synthesis. The calculations and the set-up is controlled by an instructor, so that a first synthesis can be performed. Two to three syntheses (in 3 to 4 sessions) are realized, depending on the yields or because one of the attempts may fail. The students have access to SEM when they have a minimum of two samples. A full session is dedicated to this technique, where the students are first introduced to the device and then they are trained by an instructor, which allows them to observe their first sample, and left alone to observe their remaining sample. Another full session is dedicated to powder XRD and data analysis with the help of the software Mercury. The last 1 or 2 sessions are dedicated to FTIR spectroscopy and TG analysis, as well as to exploitation of the collected data.

3. Results and Discussion

ZIF-8 is known to be a colorless powder made of polyhedral particles [3]. The polyhedral morphology of the particles is verified by SEM, and Figure 2 shows three different ZIF-8 samples prepared by different students. Most of the particles are polyhedral, and few have a regular shape (rhombic dodecahedron morphology, for example). The particles are heterogeneous in size. The sizes vary from 120 to 280 µm, 100 to 200 µm, and 60 to 260 µm, for the SEM images from top to bottom. This is in line with the particles size of 150-200 µm reported elsewhere [10].

ZIF-8 is crystalline, which can be verified by powder XRD. At this instance, the students are also introduced to the software Mercury from the Cambridge Crystallographic Data Centre [11], an easy-to-use tool that allows visualizing a crystal structure in 3D, generating a powder pattern, and defining Miller planes, for example. To that end, the students have to search for the crystallographic information file (CIF) of ZIF-8, which is available on-line [12]. Figure 3 shows the powder XRD pattern of ZIF-8. The students are first encouraged to compare it to other patterns reported elsewhere (by doing an image search via an Internet search engine using the keywords “ZIF-8 XRD pattern”, for example). The students are then introduced to Mercury (see SI) that is effective in visualizing crystal structures along the unit cell axes. Images can be saved (Figure 4 as an example) to be used as illustrations for the poster they have to prepare after completion of the experiment. The diffraction peaks of their powder pattern can be indexed with the appropriate Miller planes (Figure 3). The structure information (triclinic, space group *P*1, a = 14.7363 Å, b = 14.7801 Å, c = 14.7640 Å, α = 109.6102°, β = 109.4692°, γ = 109.3564°) can be collected. In doing so, the students are able to confirm (or not) the successful synthesis of ZIF-8.

The coordination of Zn^{2+} with 2-methylimidazole through the N atoms can be further evidenced by FTIR spectroscopy, since the Zn–N stretching mode is featured by a strong band at about 420 cm^{-1} [13]. Figure 5 shows the FTIR spectrum of ZIF-8 synthesized in our laboratory. There is a strong sharp band peaking at 421 cm^{-1} due to Zn–N bonds. The other bands at higher frequencies are ascribed to the 2-methylimidazole ligands [14].

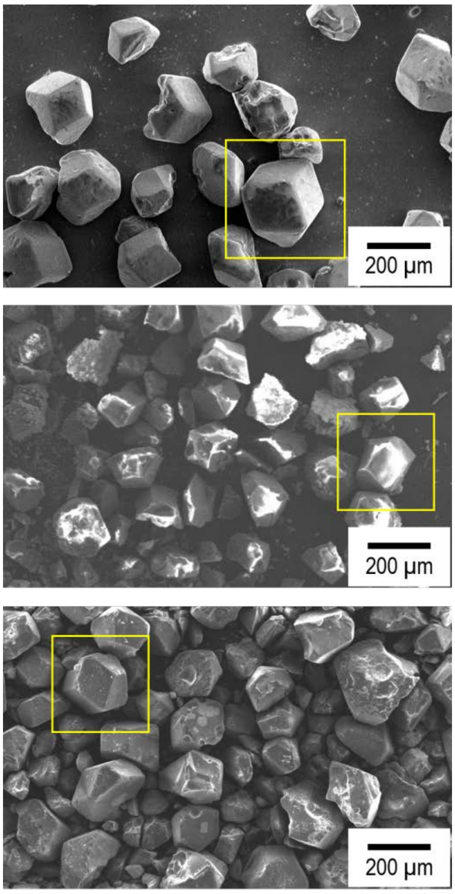

Figure 2. Three examples of ZIF-8 synthesized by the solvothermal method using DMF as solvent. The crystals with rhombic dodecahedron morphology are shown in a square with a yellow border

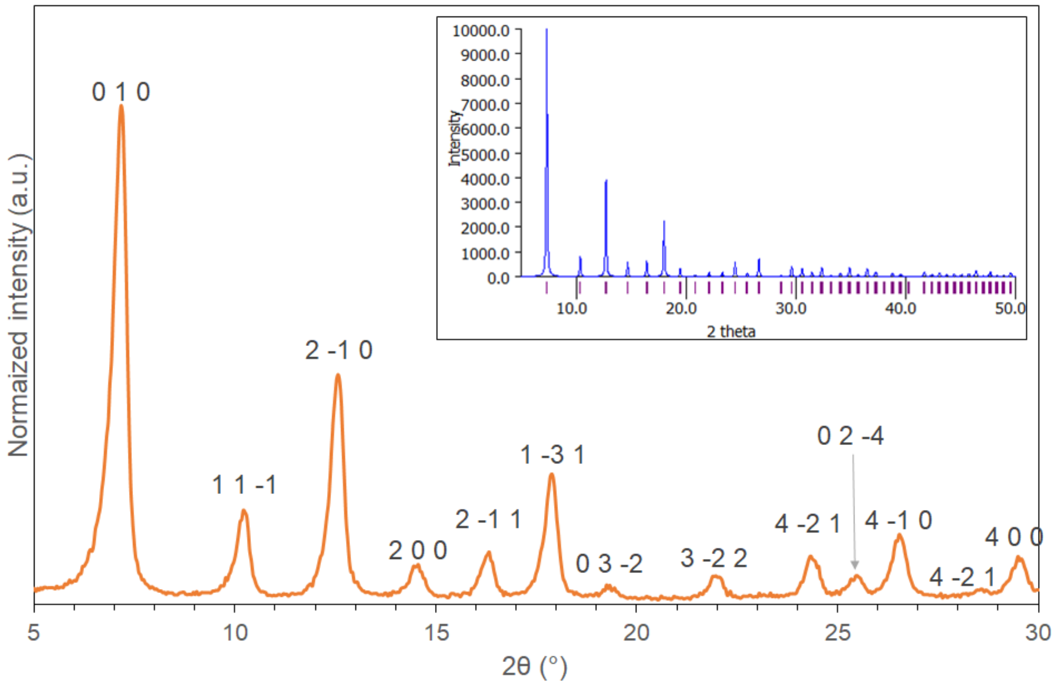

Figure 3. Powder XRD pattern of ZIF-8. The peaks were indexed with the appropriate Miller planes by using the CIF of ZIF-8 and the Mercury software, as mentioned in the text. The insert shows the pattern generated by Mercury from the CIF of ZIF-8, for comparison with the experimental powder XRD pattern

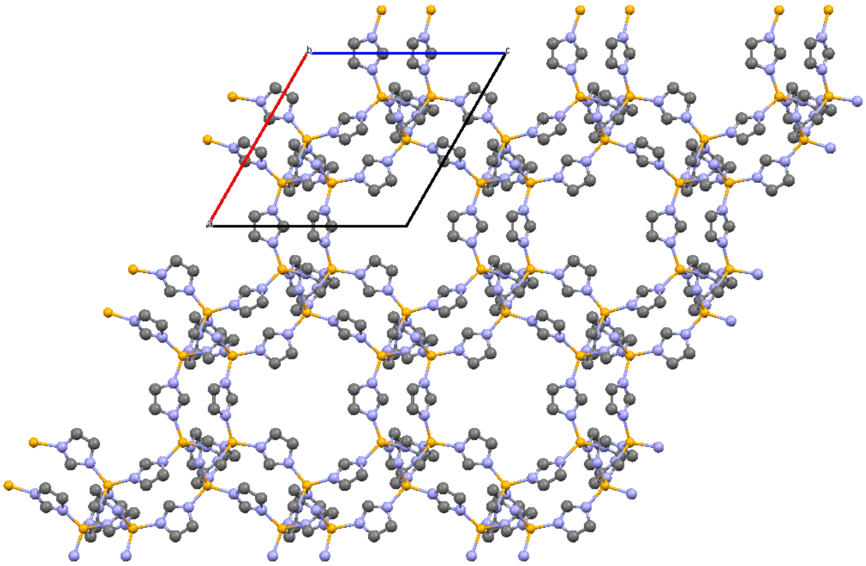

Figure 4. Crystal structure of ZIF-8 viewed along the a axis, and showing an unit cell (parallelogram with sides in red, blue and black colors). For clarity, the hydrogen atoms are not shown. The orange, violet and grey spheres represent the zinc, nitrogen and carbon atoms. Drawn by using the CIF of ZIF-8 and the Mercury software

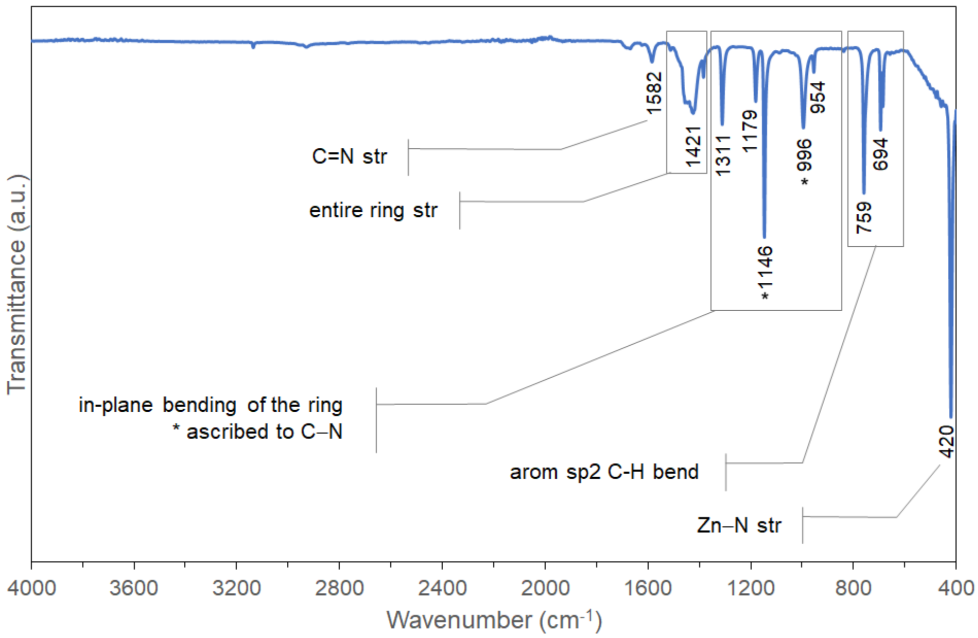

Figure 5. FTIR spectrum of ZIF-8

The thermal stability of ZIF-8 under argon can be controlled by TG analysis (Figure 6). Before the analysis, the students determine the analysis conditions based on the open literature, where it is reported that neat ZIF-8 is stable up to about 300°C and it decomposes up to about 600°C [15,16,17]. Accordingly, the TG analysis is performed with more than 10 mg of ZIF-8 sample, between 50 and 700°C, and with a heating rate of 10°C min^{-1}. In our conditions, ZIF-8 is stable up to about 300°C. Above this temperature, it decomposes and shows a weight loss of 56.6 wt% at 610°C. This is consistent with the TG results reported in the references mentioned above. There are slight differences in terms of the onset temperature of decomposition, the temperature at which the decomposition ends, and the weight loss, which can be easily explained to the students because of differences in the experimental conditions (discrepancies in the heating rate and the flow rate of the inert gas mainly). Through a discussion based on the TG curve, the students are theoretically introduced to other techniques that could be coupled to the TG analyzer in order to identify the decomposition gases (namely, gas chromatography and mass spectrometry, as well FTIR spectroscopy), as well as to carbonization of ZIF-8 under inert atmosphere [18]. Briefly stated, ZIF-8 can be synthesized in a quite easy way and in safe conditions, which allows undergraduate students producing enough material for verifying the successful synthesis and its thermal stability by using various analysis techniques such as SEM, powder XRD, FTIR spectroscopy, and TG analysis. Such a laboratory experiment could be adopted in another laboratory as it is, or through adjustments.

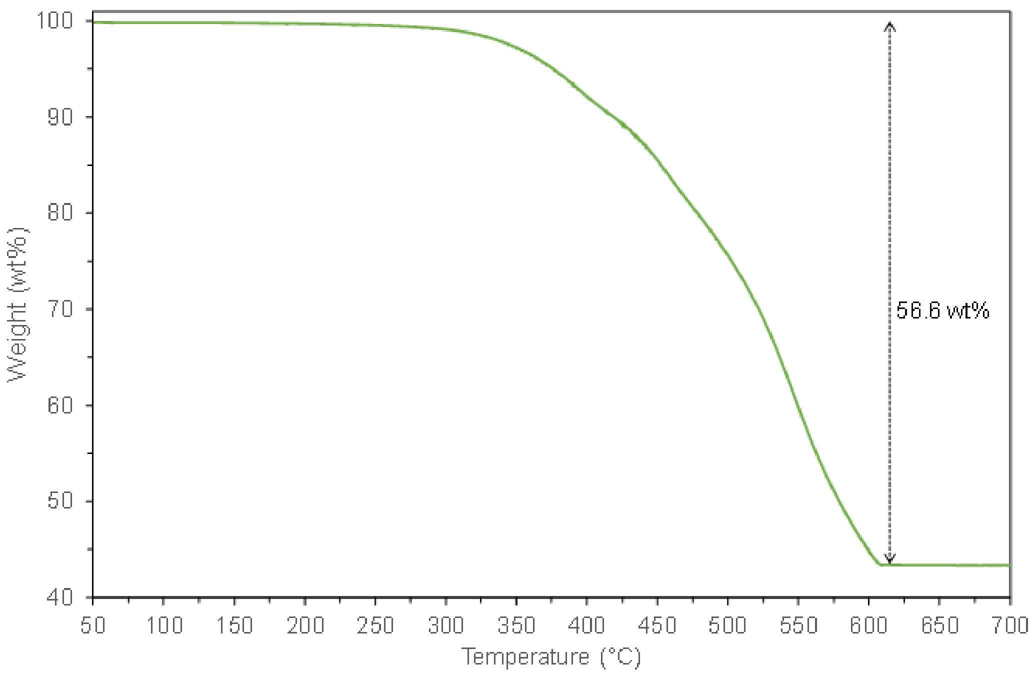

Figure 6. TG analysis of ZIF-8: 14.336 mg of sample in a platinum crucible; temperature range 50-700°C; heating rate 10°C min^{-1}; under argon flow at 20 mL min^{-1}. The weight loss of 56.6 wt% occurring between about 300 and 610°C is given

4. Perspectives of Adoption in another Laboratory

Our laboratory experiment can be adapted by other laboratories with different equipment. If there are restrictions in terms of access to SEM and/or powder XRD, or in terms of number of laboratory sessions, the experiments can be reduced. For instance, SEM can be substituted by optical microscopy (with magnification up to 1000×) or it can be omitted. With respect to powder XRD, it could be abandoned while paying more attention on the computational approach using the CIF of ZIF-8 available in the open literature. Another way to adapt the experiment is to consider alternative analyses and experiments. An example is related to the porous nature of ZIF-8 [10]. The N_2 absorption/desorption method (not available in our laboratory) can be used to determine the textural properties (specific surface area, pore volume, and pore diameter) of ZIF-8. Briefly stated, our laboratory experiment offers opportunities to be adapted by another laboratory that is equipped with some of the aforementioned techniques. However, it is worth keeping in mind that not all of the laboratories are as equipped as our laboratory or, if equipped, they do not allow students getting a full access (techniques only used by qualified technicians). The suggestions made above for replacing SEM and XRD can be considered. If the TG analysis is not possible, and if a furnace is available, the weight loss can be checked by weighting the sample before and after pyrolysis up to 650-700°C. In the case where none of the techniques are available to the students, but they are available to staff members, it is suggested to provide to the students a few SEM images, the powder XRD pattern, the FTIR spectrum and the TG curve and help them to analyze the provided data.

5. Conclusions

This inorganic chemistry laboratory experiment was designed to allow third-year undergraduate chemistry students to discover a MOF experimentally. ZIF-8 was selected because it is easy to synthesize, and the students appreciate this because they produce enough material for the analyses. In this way, the students are introduced and gain experience in solvothermal synthesis, coordination chemistry and MOFs via the synthesis of ZIF-8, SEM, powder XRD and the Mercury software, FTIR spectroscopy, and TG analysis. They are trained to use the analysis techniques independently, because one of the objectives of our laboratory experiment is to develop the autonomy of the students. They are strongly encouraged to analyze the collected data based on the open literature prior to any discussion with their instructor. This gives them an idea of what academic research is, and helps in choosing between a research master's degree and a professional master's degree to continue their studies in higher education. After 7 sessions of 4 h each in the laboratory, students have 2 sessions of 4 h each for preparing and finalizing a poster summarizing their work. During the 10^{th} and last session, the students have to present their poster orally to a jury of four instructors, who ask questions and evaluate their work. In the end, the students gain experimental independency, and this is much appreciated. A last point to mention is that the present laboratory experiment can be adapted by other laboratories. This could be envisaged in different ways: by using only one or few of the mentioned techniques, by using alternate techniques (optical microscopy instead of SEM for example), or by directly providing all of the collected data to students.

Supporting Information

Details about the teaching, instructor notes, and student's instructions are provided in the online supporting file.

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Supporting Information

The teaching in the context of our laboratory

Context

The laboratory experiment, done within the teaching unit entitled *projets tuteurés chimie*, in English, chemistry tutored project, is aimed at third-year undergraduate chemistry students who have chosen the option "science of matter" where inorganic and materials chemistries predominate. I, Demirci, am in charge of the teaching unit.

The laboratory experiment is preceded, in fall, by a bibliographic work that is done within the teaching unit also entitled *projets tuteurés chimie*. A colleague is in charge of it. The pedagogical team is composed of 8 to 12 instructors. The students search the literature associated with the topic of their future laboratory experiments. To this end, the instructors provide to the students the title of the experiment as well as a summary of 4-5 lines containing the relevant keywords. Over a period of about 10 weeks, the students, with the support of their instructors, prepare a literature survey (20-page report) which aims at introducing the experiment.

Organization of the teaching unit entitled *projets tuteurés chimie*

The teaching is structured upon around 10 sessions of 4 h each. The first 7 sessions are dedicated to the syntheses and analyses. It is worth mentioning that during the 1st session, the instructors introduce the laboratory, and give the necessary instructions, experimental procedures and work program. The 8th and 9th sessions are dedicated to the poster preparation. The instructors help the students to prepare the structure and content of the posters. The students work on their poster with the objective to finalize and print them in format A0 by the end of the 9th session. The 10th session is dedicated to the examination. The students orally present their work with the help of the poster (see hereafter).

Poster as post-laboratory work

The students prepare a poster that is part of the examination. The poster is expected to summarize the laboratory experiment. It must include a title, the names, an introduction, an experimental section, the main and most relevant results, a brief conclusion, and a list of references. Other instructions regarding the poster preparation are as follows: the logos of the University and Faculty of Science are placed at the top of the poster; the code HLCH602 of the teaching unit is given; images and graphs have priority over tables and text; the size of the images/graphs and the font size are large enough to be easily read by the jury (located at 3-5 m from the board); colors must be used.

Examination and final mark

The students present, with the help of the printed posters, their laboratory experiment to a jury composed of 4 instructors (including myself). The whole class is present and participates as described below.[1] The presentation does not exceed 10 minutes. It is followed by 10 minutes of discussion with the jury and 5 minutes of discussion with the class (in a question and answer format).

Students are evaluated as follows: 5 points for the poster (respect of the recommendations, use of space and color(s), quality of figures, spelling, etc.) and the use they make of it during the presentation; + 5 points for the oral presentation (vocabulary, terminology, visual interaction with the jury and the class, proper transitions between the paragraphs, etc.); + 10 points for the discussion with the jury and the class[1] (students are primarily assessed on the learning goals of the laboratory experiment, the concepts introduced, and the safety issues). The score for the presentation is out of 20. An additional mark, out of 20, is given by the instructor to assess the work of the student as a whole. The criteria for evaluation are as follows: attendance, involvement, rigor and reproducibility of the syntheses/results, observance of the rules (safety, storage, cleaning, etc.), general attitude, for the major ones. The final score, out of 20, is an average of the score for the presentation and the score given by instructor.

Our chemistry laboratory

We have a well-equipped chemistry laboratory, giving us wide latitude in developing laboratory experiments in inorganic and material chemistry. We have direct access to (non-exhaustive list): a dozen fume hoods, with few being equipped with vacuum lines; all necessary equipment for synthesizing nanoparticles, complexes and coordination compounds, catalysts and electrocatalysts, oligomers and polymers, ceramics, and so forth; microwave ovens, ball-millers, and furnaces; various drying techniques such as oven, microwave oven, vacuum, and supercritical; spectroscopy techniques such as infrared (Perkin Elmer Frontier, with ATR pike GladiATR), Raman, ultraviolet-visible, and fluorescence; X-ray diffraction (Philipps goniometer and Seifert generator); thermogravimetric analysis and differential scanning calorimetry; scanning electron microscopy (JEOL JSM-6010PLUS/LA) and energy-dispersive X-ray spectroscopy. We also have an access, via another laboratory, to nuclear magnetic resonance spectroscopy (nuclei ^{1}H and ^{13}C mainly).

About the laboratory experiment about ZIF-8

We initiated the inorganic chemistry laboratory experiment in the academic year 2017-2018, and twelve third-year undergraduate chemistry students successfully experimented it since then:

- *2017-2018*: Mrs. Gözde Öney, Mr. Sofian Benarib, Mr. Thomas Barral
- *2018-2019*: Mr. Loic Banaigs, M. Maxime Maréchal, Mr. Thomas Di Rito
- *2019-2020*: Mrs. Marie Brun, Mrs. Mathilde Moderne, Mrs. Safa Laraki
- *2020-2021*: Mr. Kevin Brouchier, Mr. Pierre Plaza-Joly, Mr. Yann Weinum

Instructor notes

Objectives

The first objective of the laboratory experiment is to introduce students to coordination chemistry, metal organic frameworks (MOFs) via the ZIF-8, the solvothermal synthesis method, and advanced characterization techniques such as scanning electron microscopy, powder X-ray diffraction, Fourier transform infra-red spectroscopy, and thermogravimetric analysis. The second objective is to train students to search the relevant literature, prepare their experiments based on published results, analyze and exploit their results on the basis of their knowledge and on published results, document their work relevantly, and present their work in a structured and comprehensive way (in the form of a poster).

[1] Except in 2020 and 2021 because of the sanitary crisis. In 2020 (lockdown), students did not make an oral presentation, and the final mark was only based on the assessment of the posters. In 2021, students were examined as mentioned above, the only restriction being that the whole class did not attend to all of the presentations.

Work plan

There are 10 laboratory sessions of 4 h each, with 7 dedicated to experimental work (syntheses and analyses) such as:

- *Session 1*: The students prepare the chemicals and the material, and work on the calculations for a first synthesis; the calculations and the set-up have to be controlled by the instructor, so that a first synthesis can be performed.
- *Sessions 2 to 3 or 4*: Two to three syntheses (in 3 to 4 sessions) are realized, depending on the yields or because one of the attempts may fail. With about 300 mg of ZIF-8, the students can perform and repeat all of their analyses.
- *Session 4 or 5*: Students have access to SEM only when they have at least two samples from two different synthesis batches. A full session is dedicated to this technique, at which the students are first introduced to the device, and then trained by an instructor that allows them observing their first sample. They are left alone for observing their remaining samples.
- *Session 5 or 6:* Another full session is dedicated to powder XRD and data analysis with the help of the software Mercury.
- *Sessions 6 and/or 7*: The last one or two sessions are dedicated to FTIR spectroscopy and TG analysis, as well as to exploitation of the collected data. Generally, the students have time to repeat the analyses.

Fallback solution

The students must have a good ZIF-8 sample after the first three sessions. A good sample is a material that allow students saving acceptable SEM images and collecting XRD data. If they cannot, the instructor can provide at the third or fourth session, a sample of a previously synthesized ZIF-8 (and well characterized). This will allow students performing the SEM, XRD, FTIR and TG analyses during the last sessions (as described on the previous page).

This implies that the instructor has previously synthesized a good sample of ZIF-8 (1 gram for example) and that the sample is stored in the laboratory.

It is worth mentioning that, in our laboratory experiment, all of the students synthesized enough ZIF-8 to collect good data from the different techniques they have used.

Student's instructions

Topic of the laboratory experiment[2]

Title: Zeolite imidazolate framework ZIF-8: Synthesis and characterizations

Summary: Zeolitic imidazolate frameworks (ZIFs) are porous materials with structures analogous to zeolites. They are built upon 4-connected nets of tetrahedral units, wherein metal ions, such as Zn^{2+}, are linked through the N atoms in ditopic imidazolate anions. Herein, we will focus on the ZIF-8 representative. You will synthesize it (by the solvothermal method), and analyze your samples by using the relevant analysis techniques. Accordingly, your literature survey should focus on the synthesis methods of the ZIF-8, and the common analysis techniques.

Pre-laboratory work

As a preliminary work, a bibliographic search and a literature survey have to be done. To do so, list the keywords for the bibliographic search, and search for and save the articles you find relevant based on their abstract. The final selection of the articles has to be done with your instructor who will help you in finding the key ones in the case where you have not found them. Then, read carefully each one of the articles while paying attention to the synthesis procedures, safety precautions and issues, analysis techniques, and database. Discuss with your instructor each of these aspects; write a report including, among others, the concepts addressed, the existing synthesis procedures for preparing ZIF-8, the properties of this MOF, the techniques generally used to analyze it, and the main database. This pre-lab work has to be very well done because the experiments you will conduct are all based on published results.

Laboratory experiment – Synthesis

The synthesis of ZIF-8 is based on the procedure described in details in the following reference (including the *supporting information* file attached to it):

Lee, Y. R., Jang, M. S., Cho, H. Y., Kwon, H. J., Kim, S., Ahn, W. S. (2015). ZIF-8: A comparison of synthesis methods. *Chemical Engineering Journal*, *271*, 276-280.

The solvothermal method using *N,N'*-dimethylformamide (DMF) is repeated. ZIF-8 is prepared as follows:

- List and then store under a fume hood the chemicals and the equipment you need for the experiment (to be controlled by your instructor).
- Check, prior to any handling, the safety data sheet of each of the chemicals.
- Weigh 670 mg of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ and transfer in a beaker.

[2] This title and this summary are provided to students so that they can prepare the laboratory experiment as reported herein.

- Weigh 187 mg of 2-methylimidazole $CH_3C_3H_2N_2H$ and transfer in the beaker containing the zinc salt.
- Add 50 mL of DMF (99%, from Analytic Labs).
- Stir the mixture until you obtain a clear solution.
- Transfer the as-prepared solution into a Teflon lined stainless steel autoclave (100 mL), and seal the autoclave (to be controlled by your instructor).
- Put the sealed autoclave in an oven heated at 140°C, where it will be heated for 24 h.
- Inform the laboratory technician about the time at which he will have to stop the heating the day after (after 24 h).
- Filter the as-synthesized ZIF-8, wash it three times with DMF and then three times with methanol, and dry it in an oven at 60°C.
- Recover and calculate the yield that should be around 40%.

Note that the synthesis has to be repeated twice or thrice for the sake of reproducibility, and for collecting enough ZIF-8 for the analyses you will do during the next laboratory sessions.

Laboratory experiment – SEM

Observations by SEM is possible when you have at least two ZIF-8 samples from two different synthesis batches. A whole session is dedicated to SEM. In the first part of the session, you are trained to prepare a sample and using the device. The sample preparation is as follows:

- Stick onto a sample holder a piece of carbon tape.
- Deposit a spatula tip of the sample onto the carbon tape.
- Flush the excess of powder with compressed air.

You are assisted to observe your first sample. In the second part of the session, you are left alone to observe your remaining samples.

- Save images of good resolution of the observations. You will make and try to keep the same scale bars for the different samples you will scrutinize.

Laboratory experiment – Powder XRD

The solids are analyzed by powder XRD. The experimental procedure is as follows:

- Grind the solid to obtain a homogenous powder.
- Place the homogenous powder on a sample holder (provided by your instructor).
- Check the literature to set the analysis conditions (2θ angles).
- Collect the XRD data.
- During the XRD data collection, search for the crystallographic information file (CIF) of ZIF-8, and introduce it yourself to the software Mercury from the Cambridge Crystallographic Data Centre.[3]

If you have not found the CIF of ZIF-8, have a look to the following article that is available on-line and that uploaded the CIF that is freely provided as supplementary information file:[4]

Lewis, D. W., Ruiz-Salvador, A. R., Gomez, A., Rodriguez-Albelo, L. M., Coudert, F. X., Slater, B., et al. (2009). Zeolitic imidazole frameworks: structural and energetics trends compared with their zeolite analogues. *CrystEngComm*, *11*, 2272-2276.

The X-ray pattern of your samples can be analyzed in two ways. In a first step, a simple pattern matching is done:

- Use the X-ray program (for example, X-Pert High Score) and database that is available (for example, X-Pert High Score Plus ICC Database) for X-ray diffractometer.
- Follow the user guide that is provided for the procedure to search the crystal structure of your solid.

In a second step, you will use the CIF of ZIF-8 and the Mercury software to get the ZIF-8 crystallographic information:

- Launch Mercury.
- File \ Open: open the uploaded CIF.
- Calculate \ Powder Pattern: the theoretical X-ray pattern is drawn in a new window, and each of the diffraction peaks is ascribed to a Miller plane.
- Save: the data will be saved to be re-used for plotting the pattern with MS Excel or Origin, together with the experimental X-ray pattern of your sample.
- Display \ More Information \ Structure Information: in a new window, all of the crystallographic information is given, including the structure, the cell parameters, the atoms positions, the bonds length, and so forth.
- Packing (bottom of the window): the crystal structure is drawn.
- a, b or c (top of the window): this allows viewing the crystal structure along the a, b and c crystallographic axes (more options are available; take time to see some of these options).
- Edit / Copy Image to Clipboard: you can get the crystal structure as an image to save.

Now, you are ready to use all of this information to plot the X-ray patterns (experimental and theoretical), to index each peak, and to analyze the crystal structure, which will be required for the poster.

[3] https://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/
[4] https://pubs.rsc.org/en/content/articlelanding/2009/ce/b912997a#!divAbstract

Laboratory experiment – FTIR spectroscopy

The coordination of Zn^{2+} of ZIF-8 with 2-methylimidazole through the N atoms can be evidenced by FTIR spectroscopy:

- Analyze your samples by FTIR spectroscopy (32 scans between 4000 and 400 cm^{-1}).
- Compare your spectra to the spectra available in the open literature.
- Index and identify each one of the bands.

Laboratory experiment – TG analysis

The thermal stability of your ZIF-8 samples under argon can be controlled by TG analysis:

- Determine the analysis conditions (temperature range, and heating rate) based on the open literature, and save a few of the articles found for comparison of your TG curve to the published ones.
- Transfer more than 10 mg of your sample in the platinum crucible provided by your instructor.
- Start your analysis with the assistance of the laboratory technician, while using the analysis conditions validated by your instructor.
- Compare your TG curve to the curves available in the open literature.