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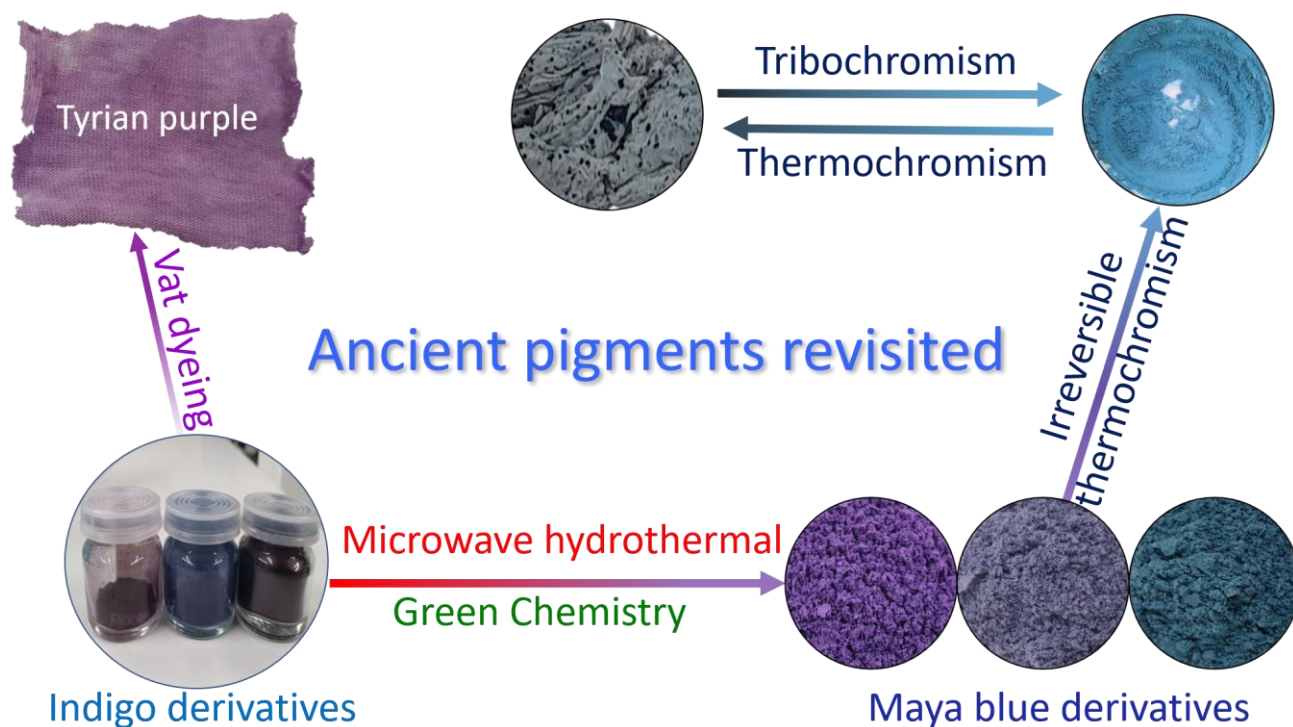
The Hunt for Maya Purple: Revisiting Ancient Pigments Syntheses and Properties

Jean-Yves Winum^{1,2}, Laurent Bernaud¹ and Jean-Sébastien Filhol^{1,3*}

1. Chemistry Department, Faculté des Sciences, Université de Montpellier, Place E. Bataillon 34095, Montpellier Cedex 5, France
2. IBMM, Univ Montpellier, CNRS, ENSCM, 34296 Montpellier, France.
3. Institut Charles Gerhardt Montpellier UMR 5253 CNRS-UM-ENSCM, Université de Montpellier, Place E. Bataillon 34095, Montpellier Cedex 5, France

ABSTRACT

Syntheses of analogues of historical indigo and Maya blue pigments using an inquiry-based approach is presented. Derivatives of indigo were synthesized (in particular Tyrian purple) and used as vat dyes for dyeing cotton or wool fabrics or mixed with a sepiolite clay to create new hues or colors of Maya blues using a green chemistry hydrothermal microwave synthesis. The hydrothermal approach allows a very quick preparation of Maya analogue pigments (typically one hour) while illustrating a green chemistry approach. The obtained Maya pigments can have very different colors (or not) from their initial indigo derivative and furthermore undergo color change under annealing (thermochromism) or mechanical grinding (tribochromism). In particular, the Tyrian purple/sepiolite chromism allows a direct visual illustration for students of the structural changes in sepiolite host-matrix associated with its pores closure and water loss.

**KEYWORDS**

First-Year Undergraduate/General, Second-Year Undergraduate, organic chemistry, Inorganic
 25 Chemistry, Inquiry-Based/Discovery Learning, Pigments, Physical Properties, Undergraduate
 Research, Hydrothermal microwave synthesis.

Historical pigments and dyes are compounds that are appealing to students as they are at the
 junction of many fields ranging from chemistry, history, industry and economy. Among them the
 30 derivatives of Indigo dye are particularly interesting. Indigotine molecule (often just called Indigo)
 extracted from *Indigofera tinctoria* was cultivated as soon as 4000 BC in Peru¹ and was also used as a
 dye in most of the antic societies from Asia to Europe.² Tyrian purple extracted from Murex family
 shellfishes (*Bolinus brandaris*, *Hexaplex trunculus*, *Hexaplex trunculus*...) was certainly one of the most
 expensive pigment during antiquity as 12000 Murex were needed to produce 1.4 g of pure dye.^{3,4}
 35 Therefore, Murex were brought close to extinction and Tyrian purple use was restricted to wealthy and

powerful people becoming in the end the color of the emperors. The dominant compound in Tyrian purple is 6,6'-dibromoindigo among others such as indigotine, indirubin and their brominated derivatives.⁵ Around 800 AD, Mayas have developed the first hybrid organic/inorganic pigment formed from a clay (palygorskite or sepiolite)⁶ processed with indigo: Maya blue is extremely resistant to weathering and chemical attack surviving hundreds of years without bleaching. Finally, from the XVIII century, indigo is the pigment used to produce the "Sergé de Nîmes" (from the south of France town Nîmes) that gave the worldwide famous Denim (a contraction of "de Nîmes") used to make blue jeans. Furthermore, for teaching, pigments and dyes synthesis also has the great advantage to give a direct indication of a synthesis success just by the involved color change. Thus, these syntheses are very good tools to gain students interest and to quickly investigate change in the reaction conditions. For more than fifteen years the "Chimie: Science Magique"⁷ program has been designing high impact laboratory experiments, involving undergraduate students in the research process.⁸⁻¹⁰ This inquiry-based approach^{7,11,12} was applied to the synthesis of Maya blue and derivatives. The classical indigo and Maya blue syntheses were initially mastered by the undergraduates during the basic training and then they were challenged in a "Genius Session" to use the acquired basic skills to find a quicker new synthesis route while making new materials, with modified properties. The global goal can be summarized into synthesizing a Maya purple mixing the Maya blue hard-wearing properties and the color of imperial Tyrian purple, by using a quick green chemistry route. To reach this goal a new microwave hydrothermal synthesis was developed that both prevents the use of strong reducers (such as dithionite) or long impregnation and drying time (typically 3-4 h) as used in classical methods.¹³ This synthesis allows obtaining Maya blue analogues after just 30 min microwave, 5 min filtration and 30 min drying. In the search of a purple analogue of the Maya blue, analogues of Indigo such as Tyrian purple were synthesized (6,6'-dibromoindigo and the 5,5'-isomer) or bought (e.g. thioindigo) and were incorporated using this route into a sepiolite clay in order to produce the equivalent of a Maya Blue with sometimes surprising results. In particular, different Maya blues with hue ranging from blue to green and a Maya purple were synthesized. Furthermore, Maya blue thermochromism and tribochromism were also shown.

COURSE ORGANIZATION

The synthesis of pigment has been performed in the bi-annual course “Chimie Science Magique: Synthèse de Matériaux à Propriétés Remarquables” by about 100 first, second- and third-year undergraduate students since 2017. The first goal of this laboratory project is for the students to learn how to synthesize dyes such as Indigo or Tyrian purple and organic/inorganic hybrid pigments similar to Maya Blue. The second goal is to develop a quicker, easier synthesis within a green chemistry approach. The final approach is to obtain a “Tyrian Maya purple” combining the color of Tyrian purple that is an Indigo derivative and the stability of Maya blue.

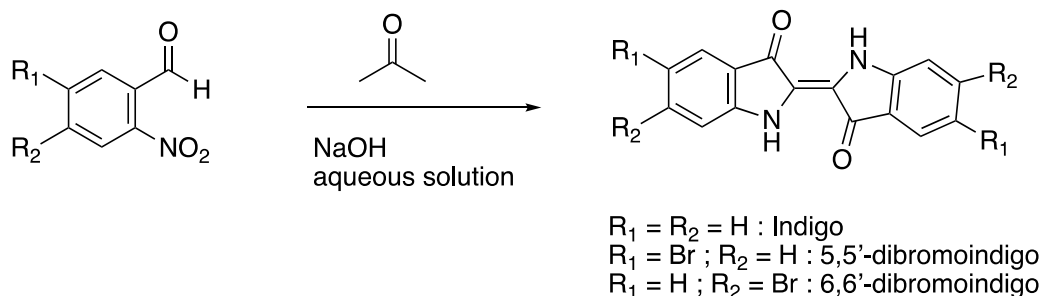
The first year of the project development, in a three-hour lab session, around 25 students are teamed into groups of two or three. Each group performs the Indigo synthesis and Maya blue using a previously published approach.¹³ They are then invited to think about what to improve in the synthesis method or which new compounds could be synthesized. In particular for the Maya blue synthesis, some bottleneck steps were identified and new synthesis were proposed to solve them. For the indigo derivatives, a protocol (and starting compounds) to synthesize Tyrian purple and 5,5'-dibromoindigo were searched in the literature. During the final “Genius Session”, different groups apply the different skills they have learnt either to the synthesis of new indigo derivatives, by using brominated initial reactant or to the synthesis of Maya blue, in order to make it faster, easier to handle, energy efficient and to produce new analogues. The last part occurs about one month later and is dedicated to a 10-15 min oral presentation, about their Genius Session, followed by 5-10 min of questioning that focuses on evaluating the knowledge acquired by the students on materials, pigment, hybrid materials and synthesis. At each new “chimie magique” session, the improvements obtained in the “genius sessions” were included in the basic training and the following genius sessions focus on new improvements. The present protocols are the result of about five course iterations.

EXPERIMENTAL DETAILS

Synthesis of indigo derivatives

All the syntheses are derived from the Baeyer and Drewsen process initially developed in 1882 (see scheme 1). They consist in the aldolic condensation¹⁴ of acetone with the derivative of 2-nitrobenzaldehyde (i.e 3-bromo-6-nitrobenzaldehyde and 4-bromo-6-nitrobenzaldehyde), followed by a

90 chain of condensation/elimination resulting in the formation of the indigo derivative (i.e. indigo, 6,6'-dibromoindigo (Tyrian purple) and the 5,5'-dibromoindigo (see Fig. 1).



Scheme 1: Synthesis of the different indigo derivatives

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In a round bottom flask of 50 mL, 0.5g (resp. 0.75g) of 2-nitrobenzaldehyde (resp. 3-bromo-6-nitrobenzaldehyde or 4-bromo-6-nitrobenzaldehyde) is dissolved in 10 mL of acetone and 18 mL of distilled water. The solution is vigorously stirred and 2.5 mL of 2 M NaOH solution is added dropwise. The color should quickly change and darken after a few minutes: the indigo (resp indigo derivatives) starts precipitating. The solution is allowed to stir for 10 more minutes before being filtered on a Büchner funnel. The obtained solid is washed with distilled water until the washing water is colorless. Then the solid is washed with cold ethanol and dried at 60 °C in a laboratory oven for one hour. A dark blue (Indigo), a purple (6,6'-dibromoindigo, Tyrian purple) and a blue (5,5'-dibromoindigo) powders are obtained (see Fig. S1 of the Supplementary Information).

105 Hydrothermal synthesis

Typically, 4 batches are prepared. Each batch contains 1g of sepiolite and 20 mg of indigo /or 32 mg of dibromoindigo (6,6'-dibromoindigo or 5,5'-dibromoindigo) /or 23 mg of thioindigo.

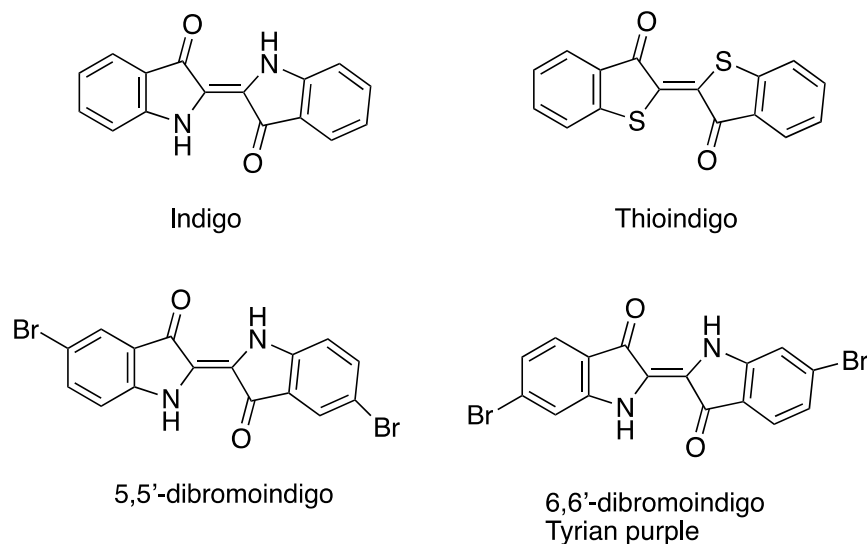


Figure 1: Structures of the different indigo derivatives.

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Each batch is grinded in a mortar and then transferred into a Teflon hydrothermal container. In each vessel, 25 mL of distilled water is added. The four containers are closed and adjusted in the microwave. The temperature is set to 195 °C and maintained for 25 min. Then, it is allowed to cool until the internal temperature reach 85 °C. The containers are then opened and the clay water mixture is quickly filtered using a Büchner funnel. The solid is then dried in an oven at 190 °C for 30 min. The resulting solid is grinded in a mortar. The powder is then rinsed using acetone to remove the trace of indigo and allowed to dry. The Maya blue derivative formation is then checked by addition of a few mL of concentrated nitric acid on a pinch of the material. The complete procedure can be found in the instructor's notes of the Supporting Information (see Fig. S3).

HAZARDS

Sepiolite: as sepiolite can contain a fraction of silica or quartz, it can be carcinogen upon repeated exposure. Safety glasses, protective gloves in combination with breathing protection (preventing dust inhalation) should be used. *Indigo* may cause irritation of mucous membranes and skin, but its derivatives toxicity was not evaluated. Thus, they should be handled with great care and exposure should remain minimal: wearing a breathing mask to prevent dust exposure is advised.

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Acetone is a flammable and irritant liquid. Gloves should be worn to reduced skin exposure and acetone vapor breathing should be prevented. *Concentrated nitric acid* is highly corrosive and its inhalation could induce lung injuries and death. It should be handled with great care, under a fume hood with maximum personal protection (appropriate gloves and eye protections....)

The Teflon containers used for the hydrothermal synthesis should be appropriate to the high temperature/pressure involved in the synthesis and remain within the operating range given by the manufacturer (as at 195 °C pressure is expected to be close to 15-20 bar). The microwave oven should also be appropriate to hydrothermal synthesis with an anti-explosion door and precise temperature and pressure controls. The Teflon container should not be opened while the internal temperature is above 80°C, as at 195 °C all the pressurized liquid water will convert into vapor instantaneously possibly causing severe burns

TEACHING AND LEARNING OUTCOMES

Background and goals

The first synthesis of Maya blue pigment occurred in 2017 in one of the genius sessions of “Chimie Magique” in a general thematic blue pigment starting from ref[13]. Maya blue was obtained as described in the literature and was then added to the standard “Chimie Magique” sessions. The students were asked to identify the possible improvements in the Maya Blue synthesis. The main improvements that were proposed were to be able to have i) other colors than blue ii) to get a faster synthesis rather than the standard one that mostly necessitates 6-7 hours because of zeolitic channel closure that was only achieved after 5 hours annealing at 190 °C, iii) improving the filtration step after indigo impregnation that was complicated as the sepiolite clay tended to plug the filter making difficult to remove the water iv) make the whole synthesis more green and energy efficient.

Water separation

The first improvement to the initial methodology was to use centrifugation to remove water from the pasty clay after indigo impregnation. A 4700 rpm centrifugation for 10 min allows the removal of the water but also of a large part of the residual indigo (not incorporated in the sepiolite) as it tends to stay at the water surface while the sepiolite is sedimenting at the bottom of the tube. Liquid phase and

supernatant indigo are removed and sepiolite is transferred into a watch glass and dried in an oven at
155 190 °C.

Indigo derivative to get new colors

In order to obtain new colors, indigo derivatives were synthesized in the “Genius session” following the classical Baeyer synthesis but with different bromated reactant. In particular the purple 6,6'-dibromoindigo was synthesized. This molecule is the main component in the historical Tyrian purple.
160 5,5'-dibromoindigo isomer was also synthesized and gives a blue compound with a slightly lighter hue than Indigo. These indigo derivatives were also used to dye cotton and wool fabrics as detailed in the instructor’s notes (see Fig. S2). Other commercial derivatives of Indigo that were known to insert in clay such as red thioindigo pigment was also used.^{15,16} Using the classical synthesis, the impregnation of sepiolite by indigo, 6,6'-dibromoindigo, 5,5'-dibromoindigo and thioindigo led respectively to the blue,
165 purple/pink, blue and red products. After the final annealing at 190 °C blue, blue, purple and blue colors were obtained, the different blues having different hues (see Fig. 2).

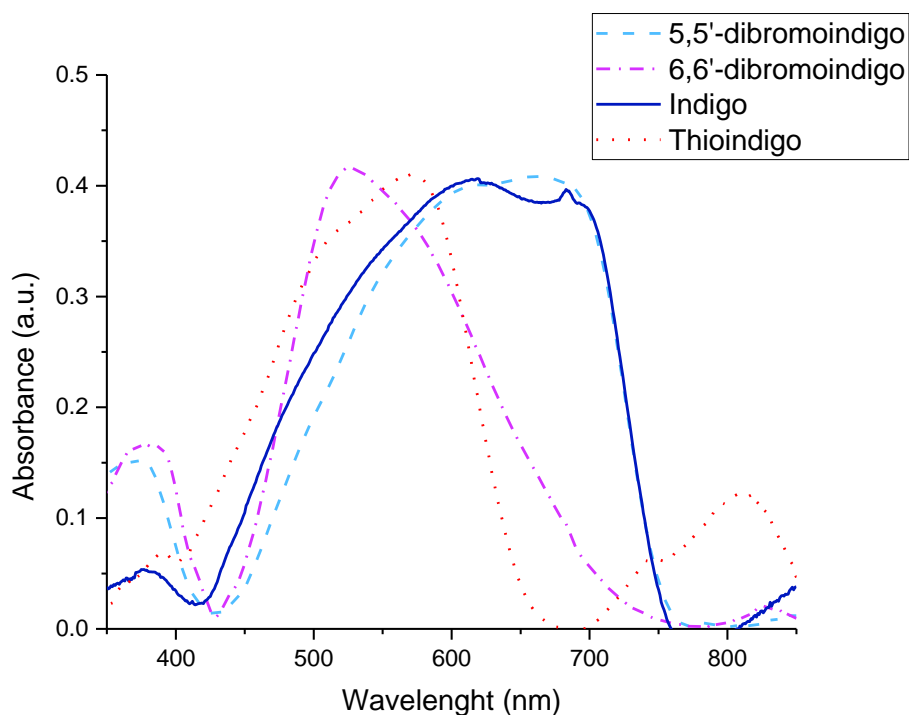


Figure 2: Reflectance UV-visible spectra of different powders of indigo derivatives obtained using an integration sphere. The reflectance scale was converted into absorbance scale for easier interpretation from the students.

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The final dehydration and zeolitic pore closing^{15,17-19} leads to an important change in color for the Tyrian purple and thioindigo that become respectively blue and purple suggesting that the cavity formation leads to a change in its chemical interaction with the sepiolite^{20,21} that induces a strong bathochromism from purple to blue (see Fig 3). The property for a material to change color with temperature is called thermochromism; in the present case as the color change is irreversible upon cooling, this phenomenon is called irreversible thermochromism. Irreversible thermochromic compounds are part of smart materials with important industrial applications as they give a permanent record of the temperature variations.²² If Tyrian purple cannot be used to create Maya purple as initially expected, it still is also a color indicator of the closing of the sepiolite pores with increasing temperature and thus an irreversible thermochrom: it is purple when the pores are open while blue when the pores are closed the following the sepiolite structure thermal changes.^{17,19} Thus, the irreversible thermochromism²³ is due to the irreversible conversion of one phase into another one as shown by the UV-Visible spectra in Fig.6 associated with some structural water loss starting as low as 120 °C but only fully completed around 190 °C as shown by the TGA in the Supporting Information (see Fig. S9)

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Figure 3: Left: Sepiolite+Tyrian purple after 140 °C in microwave for 25 min and drying for 24h at 150 °C. Right Sepiolite+Tyrian purple after 195 °C in microwave for 25 min and drying for 24h at 195°C

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Tyrian purple was then used to quickly evaluate the pores closing as a function of the synthesis used. The students were shown that even if the initial goal to create Maya purple with Tyrian purple was

a failure, another even the more interesting property such as irreversible thermochromism allowing quick identification of sepiolite pore closure can be reached allowing a quick evaluation of the synthesis used. This initiated with the students interesting discussions about the meaning of experimental failure, exploiting apparent failure and serendipity.

Finally, after some tests, the purple Maya was obtained using commercial thioindigo, that allows reaching the “Maya purple” goal. Note that a Maya green was also obtained from indigo after some thermal treatments, that was associated with the formation at high temperature of dehydroindigo inside the sepiolite.²⁴

Hydrothermal microwave synthesis

Within the available advanced synthesis apparatus (sonochemistry, ball-milling...) after a few unsuccessful tests, the hydrothermal microwave synthesis of Maya blue derivative has turned to be the optimal solution. It is using water as a solvent, no added reductant such as dithionite is needed, nearly no byproducts are formed, it is energy efficient for heating the reactor, leads to a very fast synthesis and produces resistant pigments. The detailed microwave hydrothermal experimental procedure is described in the instructor’s notes.



Figure 4: Hydrothermal microwave Polytetrafluoroethylene (PTFE) vessel

Using a hydrothermal Teflon reactor (see Fig.4) allows to work in water for temperature up to 230 °C under a corresponding pressure of about 25 bar. At such a high temperature, the reaction kinetic are

strongly increased, but the properties of water are also strongly modified. First, at high temperature and pressure, H-bond network start to break down making water behave more and more like an aprotic solvent. Water is then also losing part of its hydration power leading to a less efficient solvation of polar molecules. Furthermore, the dielectric constant of water falls from 80 at room temperature to about 40 at 200 °C.²⁵ Viscosity and surface tension also decrease with increasing temperature²⁶ while water ionic product will increase with pK_e decreasing down to 11.5 around 200 °C . In these conditions, organic molecules become better solvated in water as exemplified by the increase of solubility of chrysene in water by a factor 10^5 at 225°C compared to room temperature.²⁷

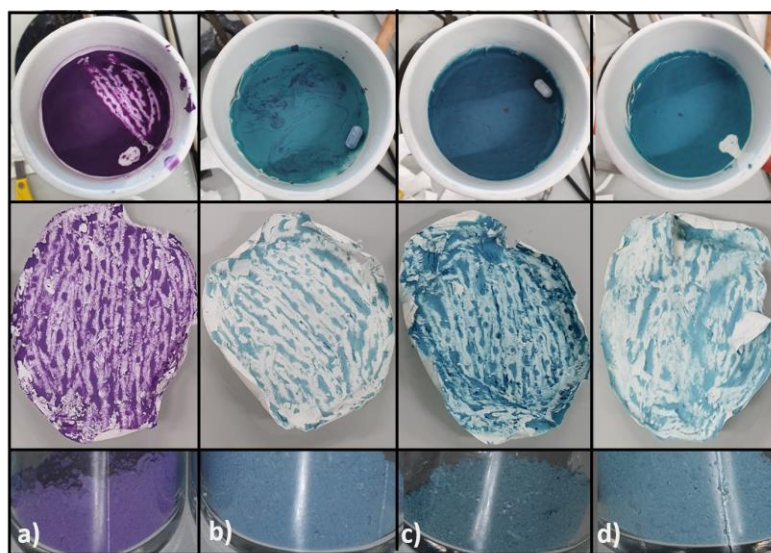


Figure 5 “Maya blues” made from sepiolite and a) thioindigo b) 5,5'-dibromoindigo c) Indigo and d) 6,6'-dibromoindigo. (Up) after filtering the hydrothermal product (Middle) after annealing the product for 30 min at 190 °C. (Down): After a second washing and drying

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This suggests that the integration of indigo derivatives into the channels of a sepiolite could be made very efficient in water by a hydrothermal approach: indigo solubility in the water media will be increased improving the transport into the sepiolite. The combination with a microwave will allow to have a very homogeneous heating preventing inhomogeneity of the indigo integration in sepiolite, a very efficient energy transfer (less than 800 W are needed to bring 4 reactors from room temperature to 195 °C in 10 min and less than 400 W are used to maintain at this temperature), and a very good temperature control

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(temperature oscillations are lower than 1-2°C). Test using 6,6'-dibromoindigo properties (color change with sepiolite channel closing) have then shown that if indigo integration is already very fast at 140°C but working at a temperature of 195 °C already allows direct sepiolite dehydration and closure of the channel thus protecting the integrated indigo molecules (see Fig.4) and formation of the Maya derivative. The channel closure can be checked by TGA and X-ray diffraction (Fig. S9 and S10), but also by immersion of the Maya derivative into concentrated nitric acid: when channels are fully closed Maya derivatives can remain colored after 5 min immersion while the pure indigo (or derivative) or the unclosed sepiolite/indigo is discolored within a few seconds²⁸ (see Fig. S6). Another advantage is after the 195 °C synthesis, the products become easily filtered using a Büchner funnel without the need for centrifugation (see Fig.5). This suggests that the sepiolite matrix change is not only limited to the internal channels but also involve the inter grain interactions making it less prone to gel creation. Using this approach allows both quick indigo derivatives integration and sepiolite dehydration in only water without the need of other chemicals and gives “Maya blue”-like pigments with different colors and hues (see Fig. 6).

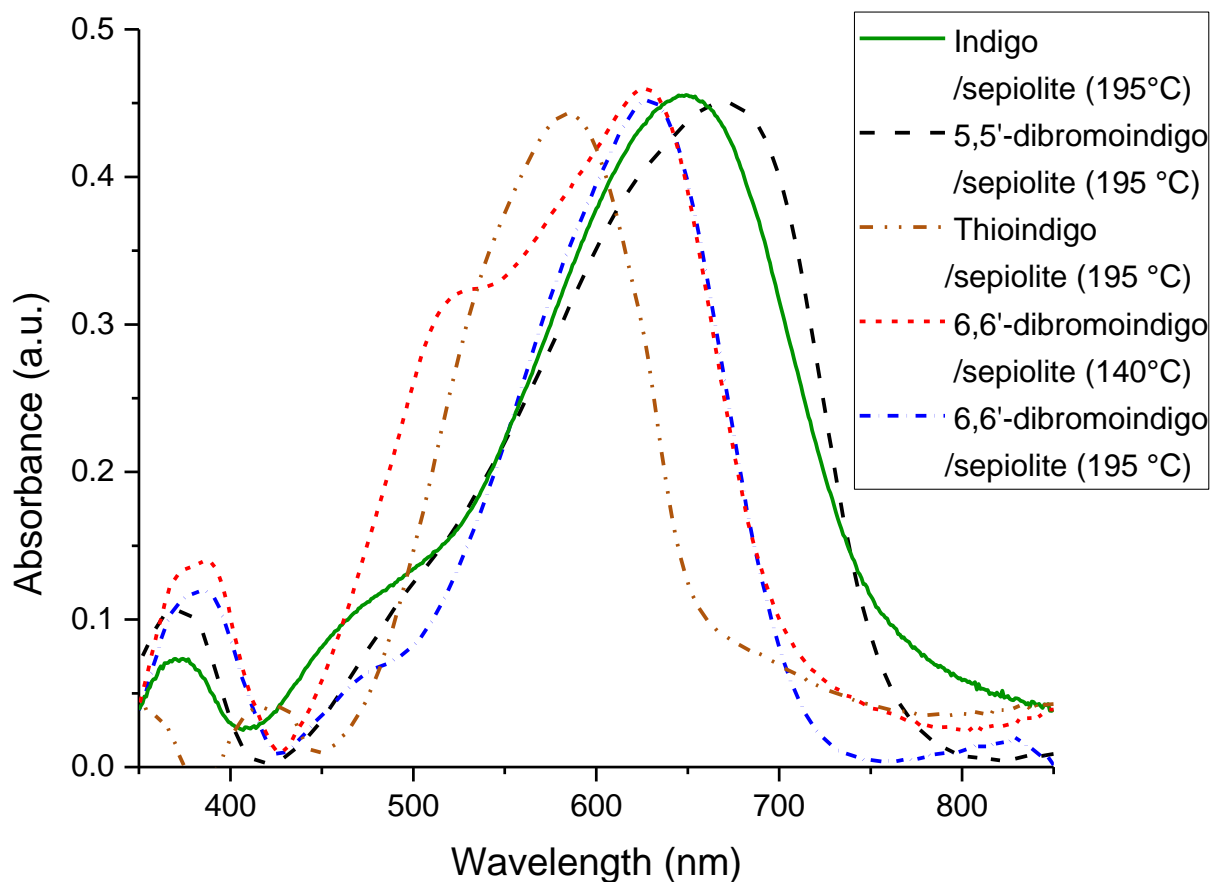


Figure 6: Reflectance spectra of solid powders of “Maya blues” from hydrothermal microwave synthesis (from sepiolite and different indigo derivatives) obtained using an integration sphere. The reflectance scale was converted into absorbance scale for easier interpretation from the students.

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Thermochromism/tribochromism

If the final drying is increased to 48h in the drying oven at 190 °C, the obtained pigments (except the one made from thioindigo) become greyish/greenish and discolored with a lighter hue. As seen in the TGA (fig. S9) and proposed in the literature,^{17,29} this is probably the consequence of the loss of a water molecule coordinating a Mg atom in the sepiolite structure; this would allow the interaction of Mg acidic site with the indigo molecules as previously suggested,²⁰ thus reducing the π -system conjugation

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and changing the color and absorptivity. When the compound is crushed in a mortar, the greenish color reverses back to the initial blue color (see Fig.7). The grinding is creating strain on the sepiolite structure, also increasing the surface of contact with air by fragmentation allowing sepiolite to re-adsorb moisture changing its color back to the original one as the Mg site exchange indigo and a water molecule.

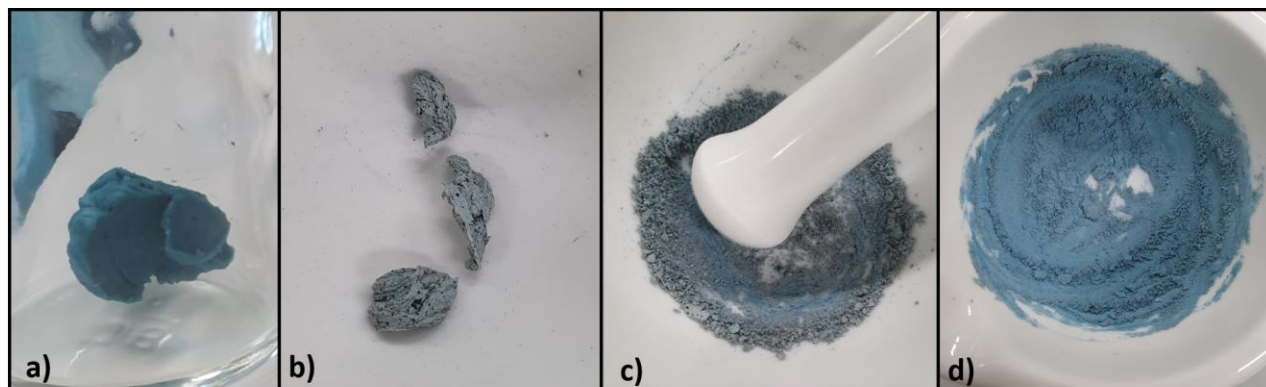


Figure 7: Evolution of Maya blue a) before a 48 h in a drying oven at 190 °C b) after the drying c) beginning of the grinding d) after 3 min grinding

Achievement of the goals

This teaching approach with first- and second-year undergraduate students proved to be very positive for both the laboratory work, and the final oral presentations. It allows introducing a green chemistry approach and the use of hydrothermal and microwave synthesizes. As the synthesis is very fast and reliable, at least four batches can be achieved in a three-hours laboratory period allowing each group synthesizing analogues of Maya blue by using mostly any aromatic pigment weakly soluble in water even beyond the indigo family, presented therein. This enables a careful monitoring of the students' laboratory skills, such as weighting large and tiny quantities, using an advanced microwave hydrothermal process, synthesizing, filtering and using centrifugation to separate liquid from solid phase, but also of the theoretical skills and knowledge such as understanding the change of water properties at high temperature and pressure, clay structure, the origin of color in indigo, the change of color induced by molecule-host interaction, chemical safety etc. The student initial knowledge on organic chemistry was also evaluated using a serious game described previously³⁰, allowing to identify weakness problem before starting the organic synthesis and was used to initiate questions to the instructors. Furthermore, the Genius session has allowed the evaluation the students' ability to transpose an experimental setup to new problems such as changing the molecules integrated in sepiolite, investigating the synthesis parameters and thermochromic or tribochromic materials. The Genius sessions were evaluated by an external board of high

school/university teachers and research staff that were always pleased to observe a high involvement of the students in both the accomplished work and presentation compared to more usual programs. The general assessment of the “Chimie Magique” approach on students outcomes was recently carefully
285 evaluated⁷ and show a very positive impact. A very specific benefit from this project is to demonstrate that in research you can start with the wrong idea (i.e. make a Mayan purple with Tyrian Purple), make the product but finally with the wrong property (because it is blue), but find a clever way to change this “failure” into a beneficial outcome (by using the color change to quickly investigate the optimal synthesis hydrothermal conditions). It illustrates the concept of serendipity that is very difficult for undergraduate
290 students used to classical lab work to understand. The difference between failure and success can just depend on the capacity to adapt and exploit the results. The developed syntheses were integrated in our basic training, but also transposed to other courses such as “projets tuteurés” in the third years of chemistry and of “physics of color”.

CONCLUSION

295 The hunt for “Maya Purple” offers to student many insights in different fields of chemistry. Firstly, it shows how modern chemistry can reproduce ancient pigments, rationalize the origin of their properties and use this knowledge to create new pigments with different colors and properties. Secondly, the microwave hydrothermal route that we propose shows an advanced synthesis technic demonstrating
300 the green chemistry stakes: only water as a solvent, low energy consumption nearly no chemical pollution and long cycle of life pigment. Finally, it also demonstrates to student what is serendipity, that initial guess such as making Maya purple from Tyrian purple can be very wrong, but can lead to even more interesting properties allowing a fast tuning of synthesis parameters.

ASSOCIATED CONTENT

Supporting Information

305 The Supporting Information is available on the [ACS Publications website](#): Student laboratory handouts, Instructor Notes with supplementary material.

AUTHOR INFORMATION

Corresponding Author

310 *E-mail: jean-sebastien.filhol@umontpellier.fr

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