IN SEARCH OF FORGOTTEN COLOUR

PHOTODEGRADATION OF HYDROXYANTHRAQUINONES ASSOCIATED WITH MORDANTS

BY:
LINH TRAN

UNDER THE DIRECTION OF:
PROF. MAGUY JABER
DR. ROMAIN BERRAUD-PACHE

Photo J; Clottes

Chauvet Cave
Red negative hand and
partial outline of mammoth

Parietal paintings, Tassili n'Ajjer, in Jabarren, Algeria

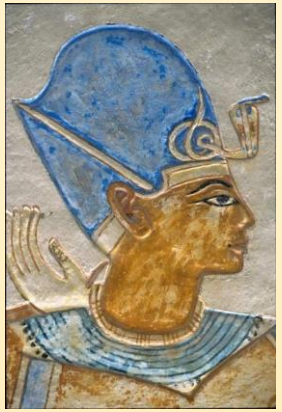
Prehistory — Antiquity — ... — 19th century

30 000 yrs

Egypt

Photo J; Clottes

Chauvet Cave
Red negative hand and partial outline of mammoth



King Ramesses III Tomb of Prince Amun-her-khepeshef, Valley of the Queens, West Thebes.

Osiris represented in green from tom Nefertari

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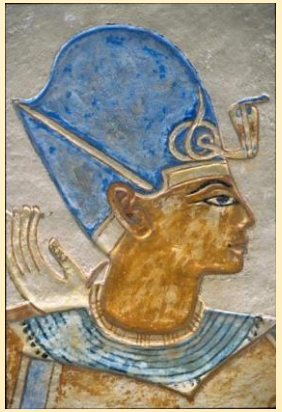

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(photo: Steven Zucker, CC BY-NC-SA 2.0)

Ravenna mosaics depicting Emperor Justinian, Ravenna, Italy

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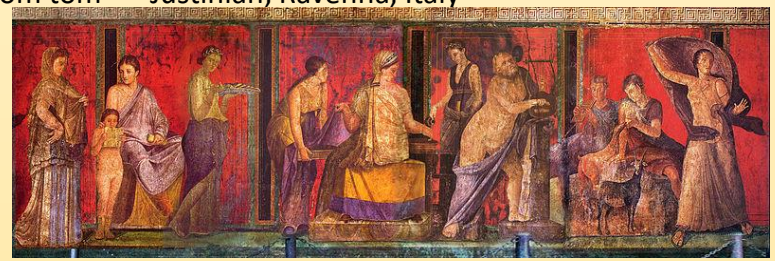

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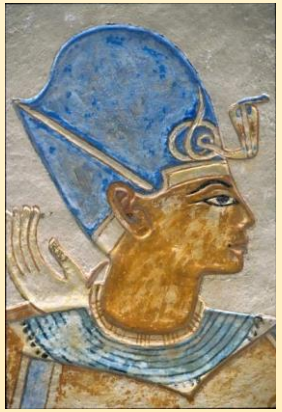

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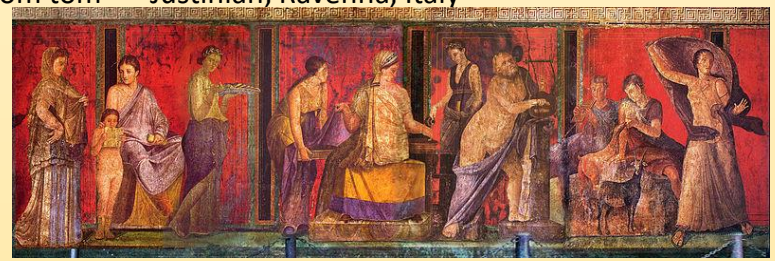

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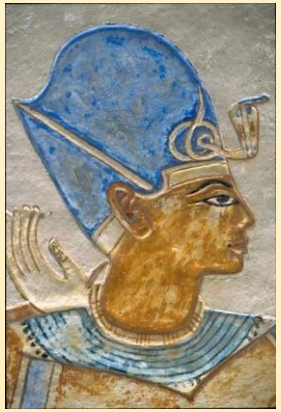

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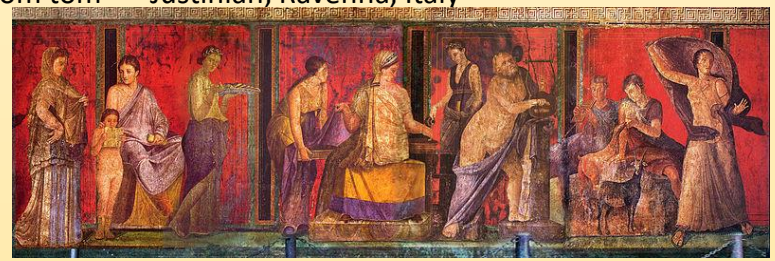

Pompei, Villa of the Mysteries

UK Queen Victoria wearing mauvein

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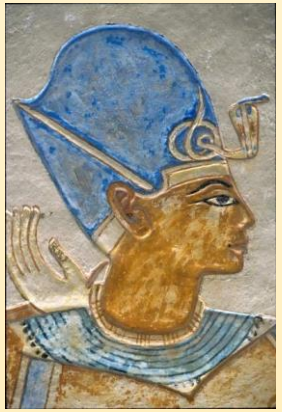

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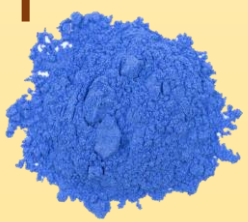
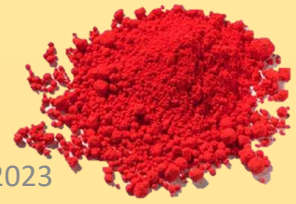
Hematite Fe_2O_3



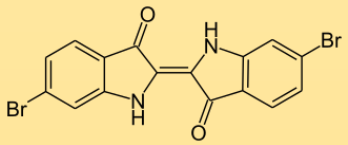
Egyptian Blue $CaCuSi_4O_{10}$

Egyptian Green $CaOCuO(SiO_2)_4$

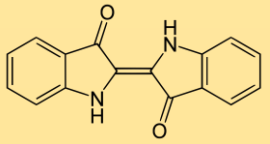
Royal Purple



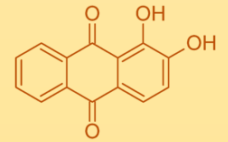
Vermilion HgS

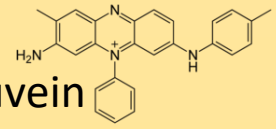


Indigo (Guede)



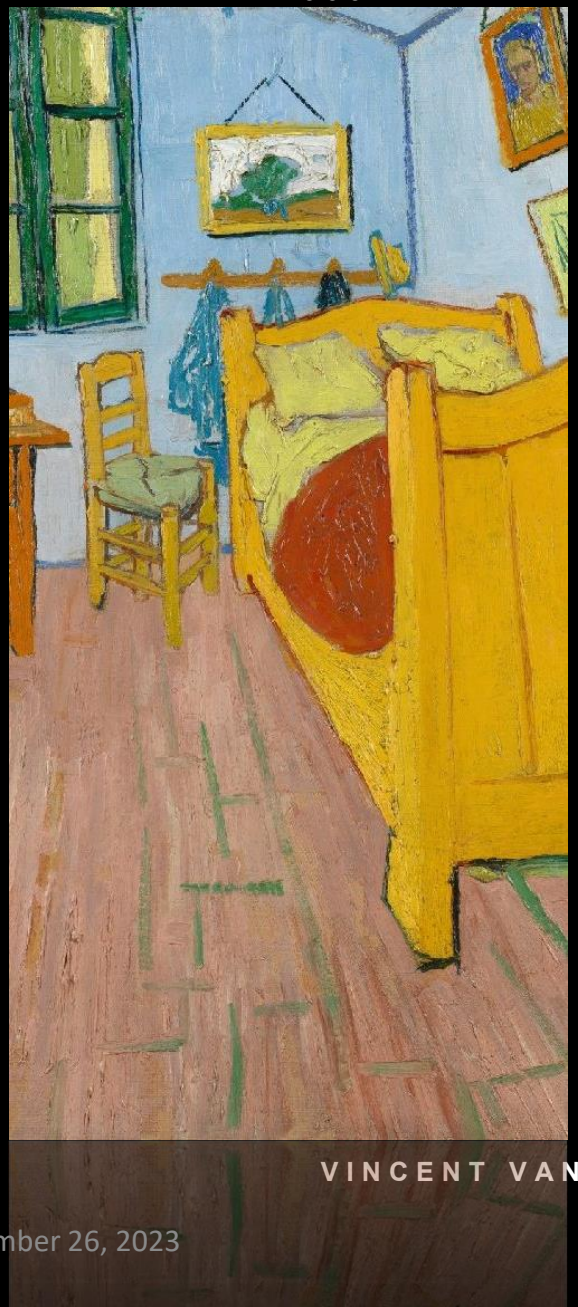
Madder



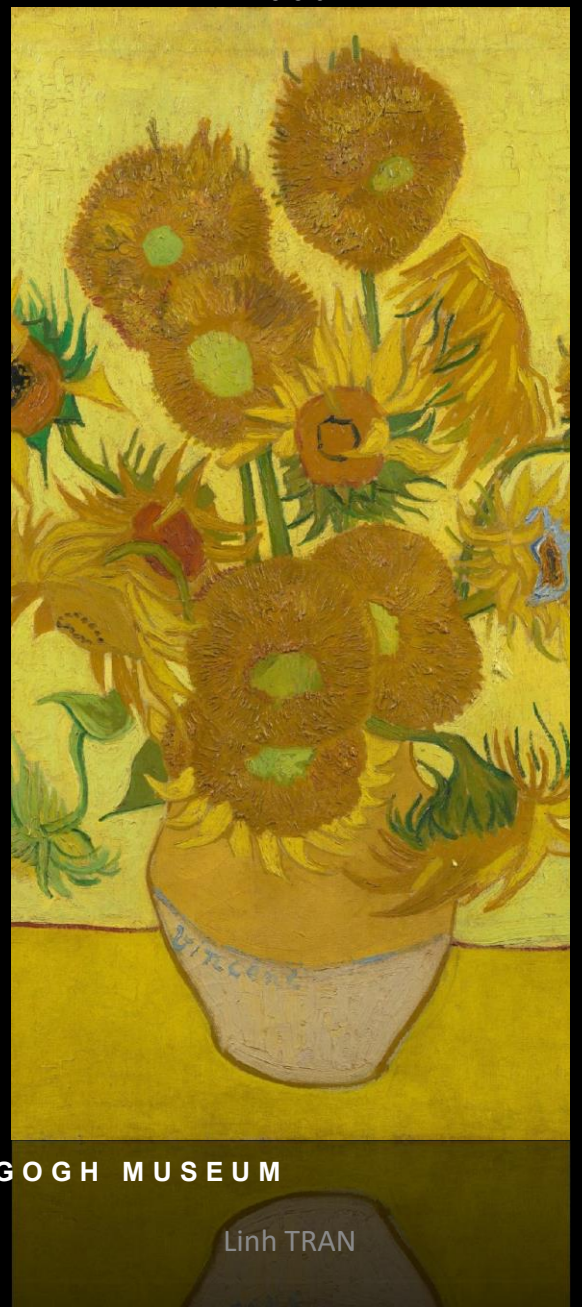


Mauvein

The Bedroom
1888



The Sunflowers
1889



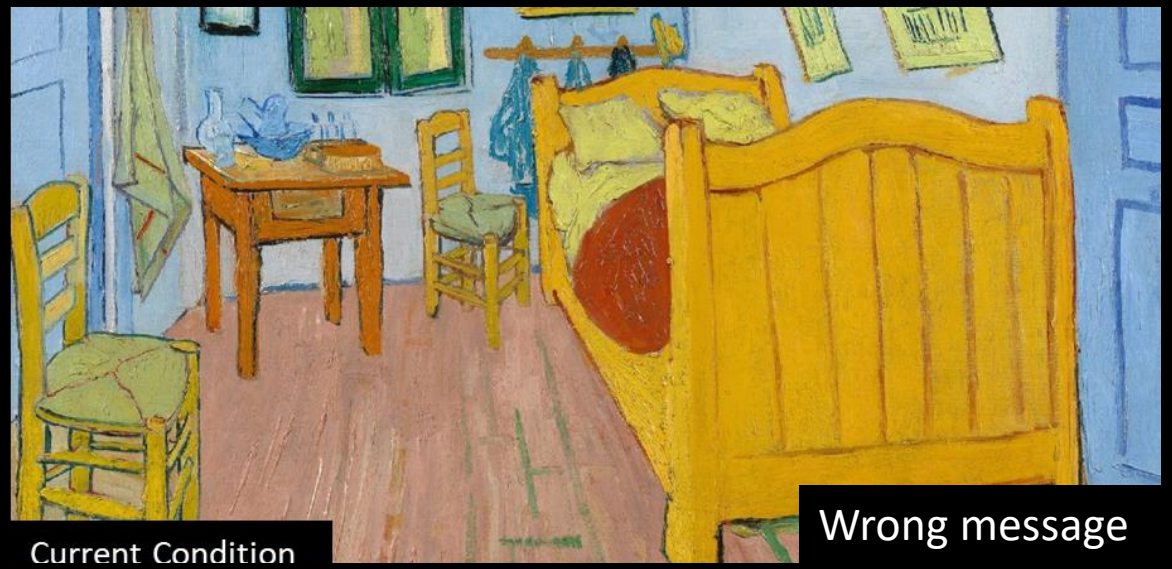
Madame Leon Clapisson
1883

VINCENT VAN GOGH MUSEUM

PIERRE AUGUSTE RENOIR
The Art Institute of Chicago, IL, USA

The bedroom, Vincent van Gogh (1853 - 1890), Arles, October 1888

Van Gogh Museum, Amsterdam (Vincent van Gogh Foundation)



Current Condition

Wrong message

Madame Leon Clapisson, Pierre-Auguste RENOIR

The Art Institute of Chicago, IL, USA Reconstruction by Northwestern University

Wrong message

Wrong message

Sunflowers, Vincent van Gogh

Liao, S., Koehl, P., Schultens, J. et al. The geometry of colors in van Gogh's Sunflowers. Herit Sci 9, 136 (2021). https://doi.org/10.1186/s40494-021-00608-y

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Simulated original appearance

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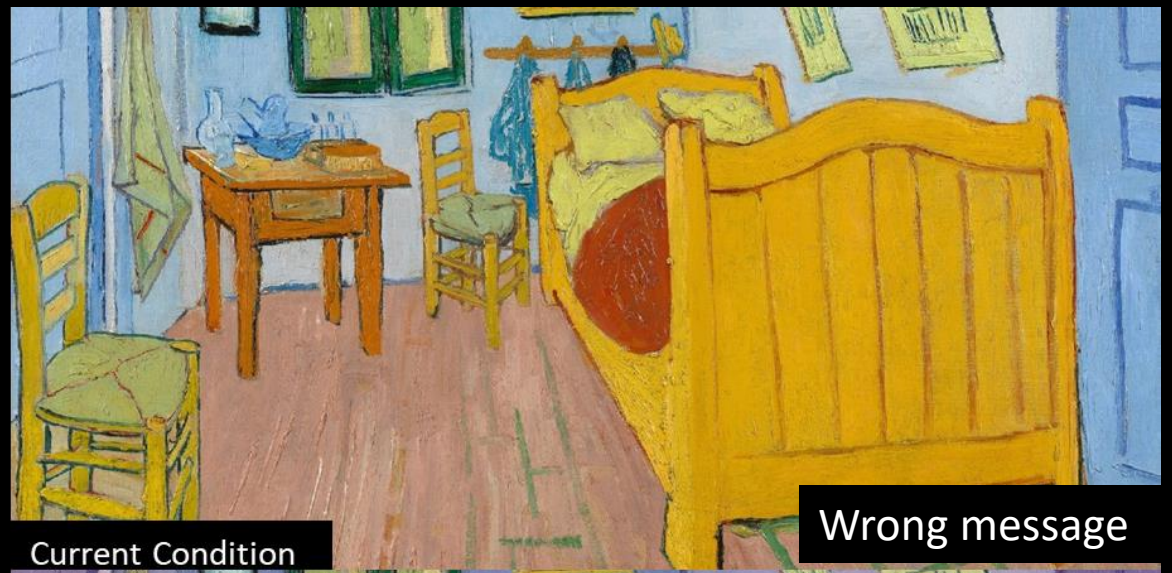

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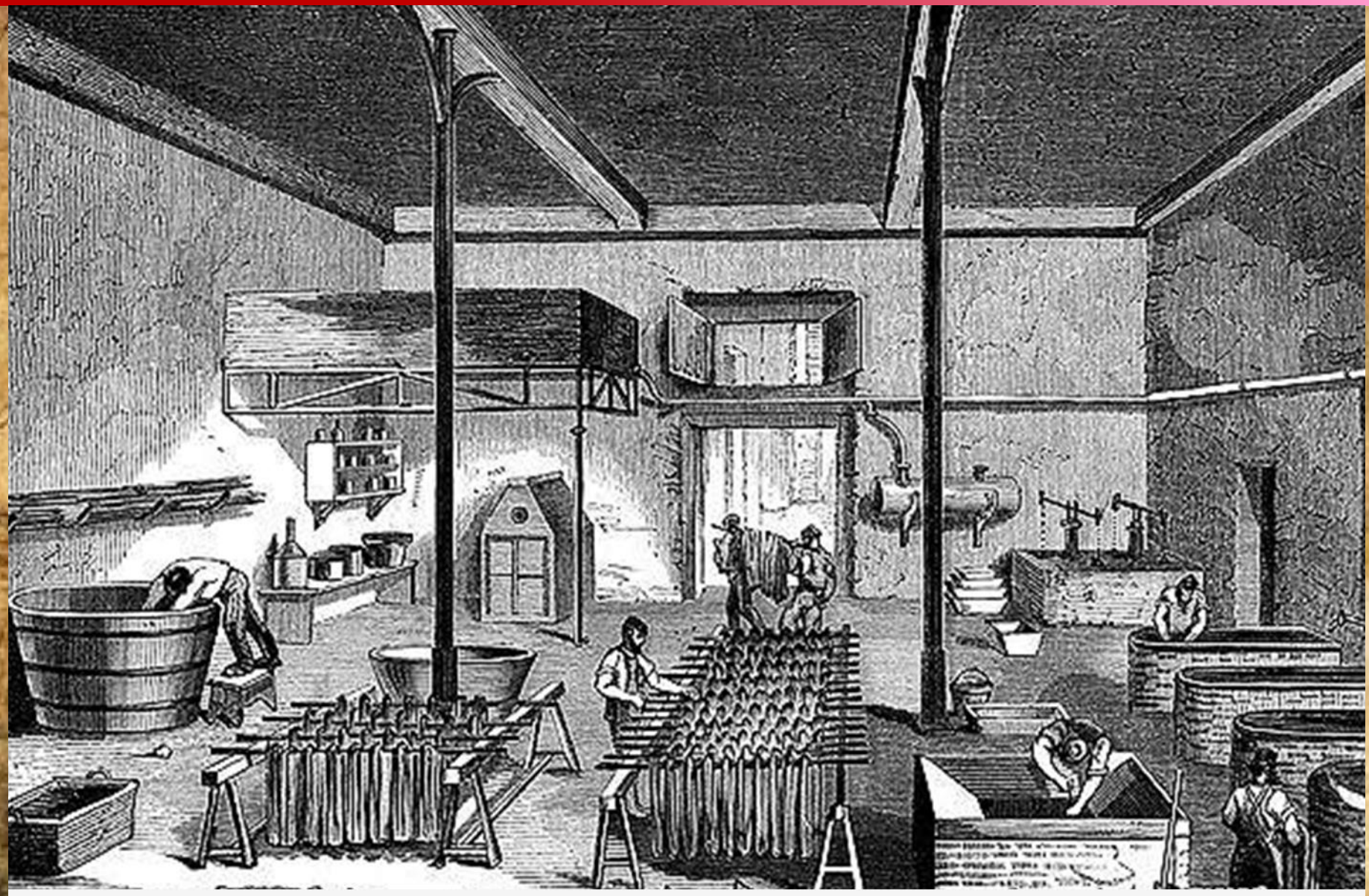
Madder

A QUICK HISTORY OF MADDER



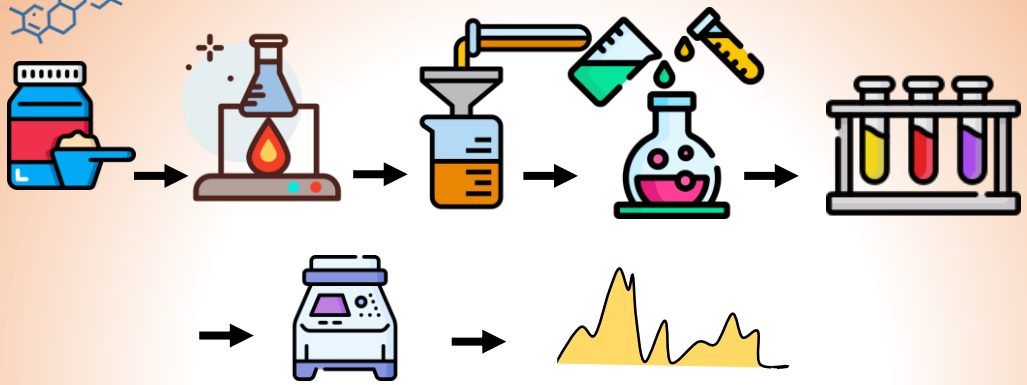
Les Gobelins, Dyeing workshop. Extr. from: "The great factories of Turgan", 1888

A QUICK HISTORY OF MADDER

Colonel, adjutant major and second lieutenant (light infantry).Extr. from: The French painted by themselves, 1840-1842.

Experimental vs. Computed

Experiment

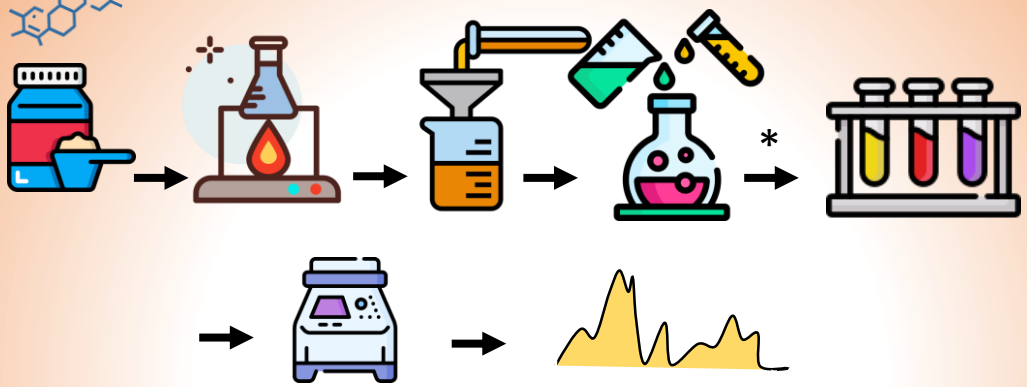


Long, costly, limited

Computation

Experimental vs. Computed

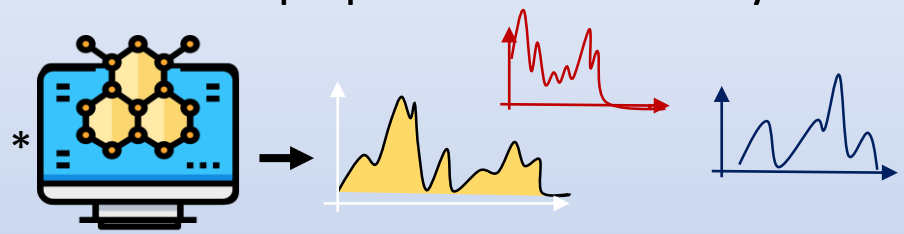
Experiment



Long, costly, limited

Computation

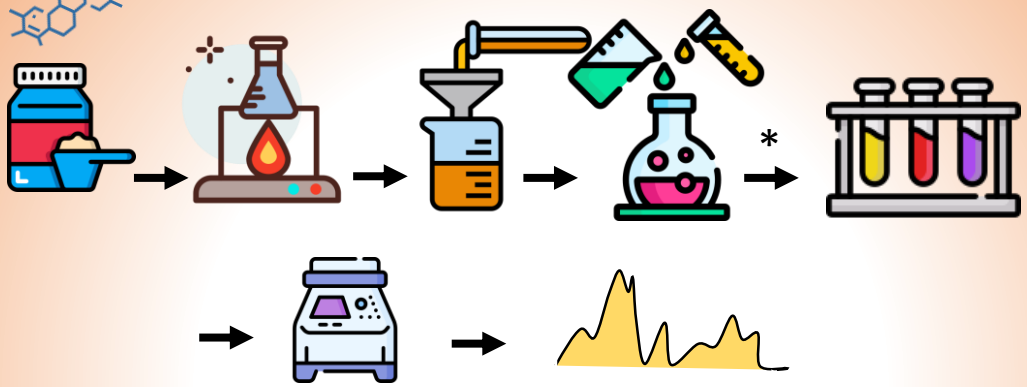
Predict different properties of different dyes



Time & cost reduced

Experimental vs. Computed

Experiment

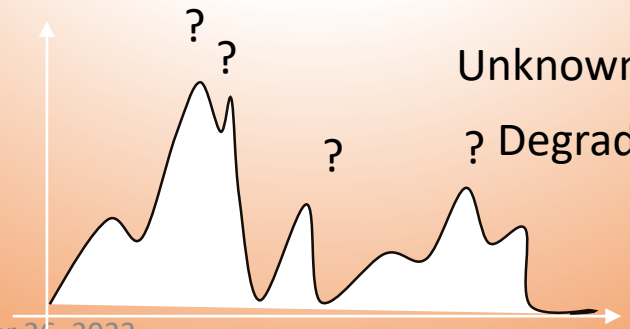


Long, costly, limited

Very complex data

Sophisticated spectroscopy Techniques (non invasive)

Mixture

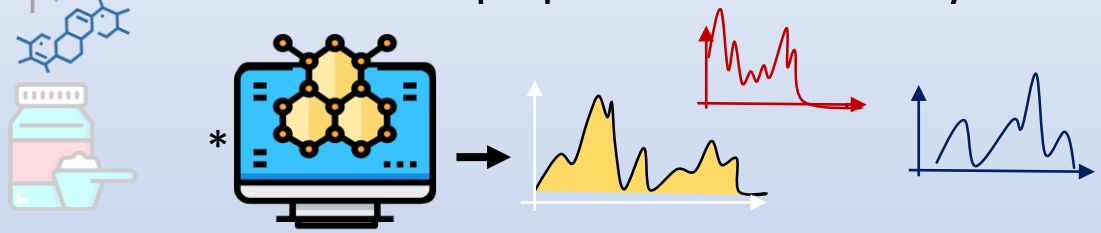


Unknown products

? Degraded products

Computation

Predict different properties of different dyes

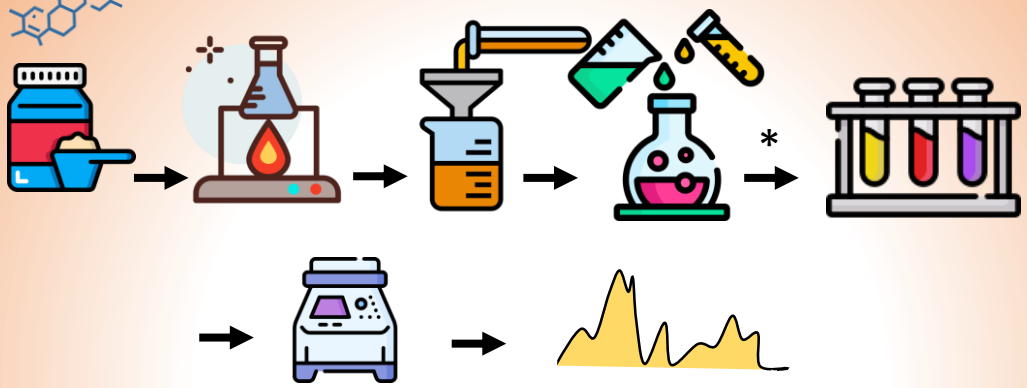


Time & cost reduced

Understand the impact of each factor individually

Experimental vs. Computed

Experiment



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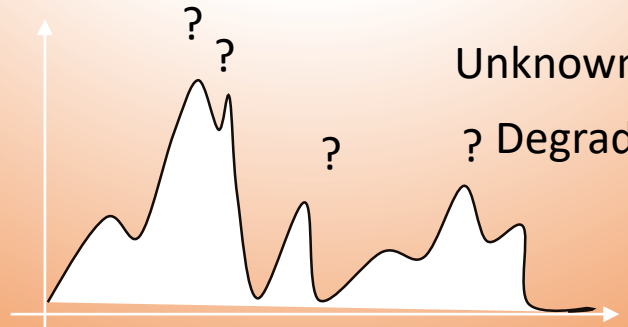
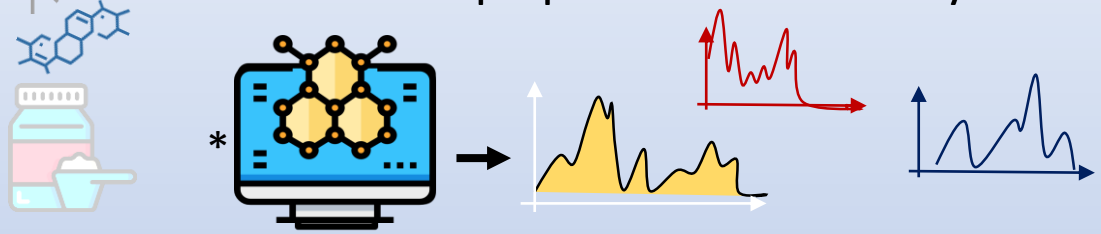


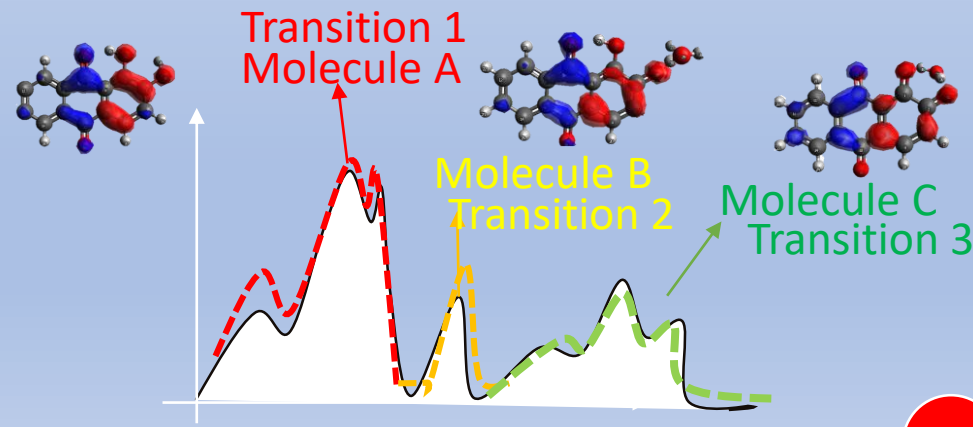
Computation

Predict different properties of different dyes



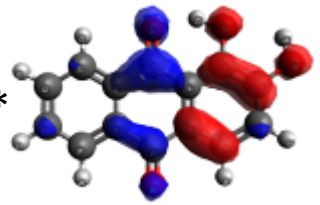
Time & cost reduced

Understand the impact of each factor individually
Understand experimental data



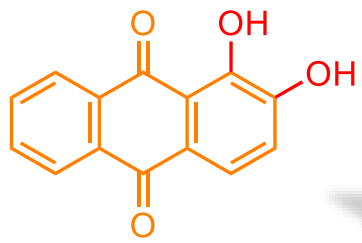
Computed vs Exp. UV-Vis spectrum Alizarin

π ->π*



pH=2.8

H_2A



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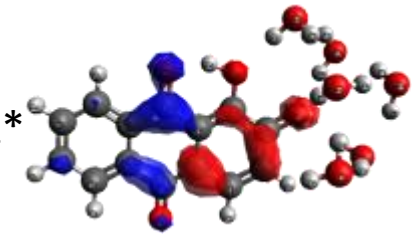
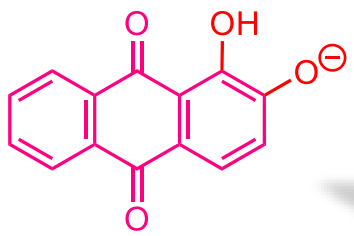


pH=8.5

HA^-



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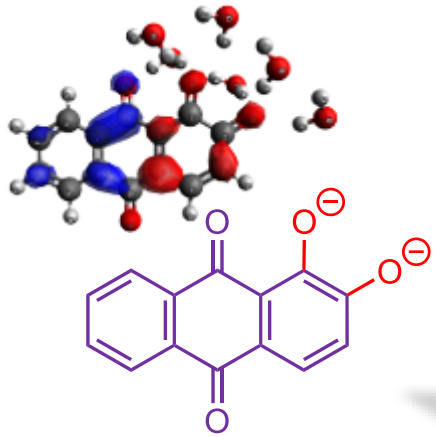
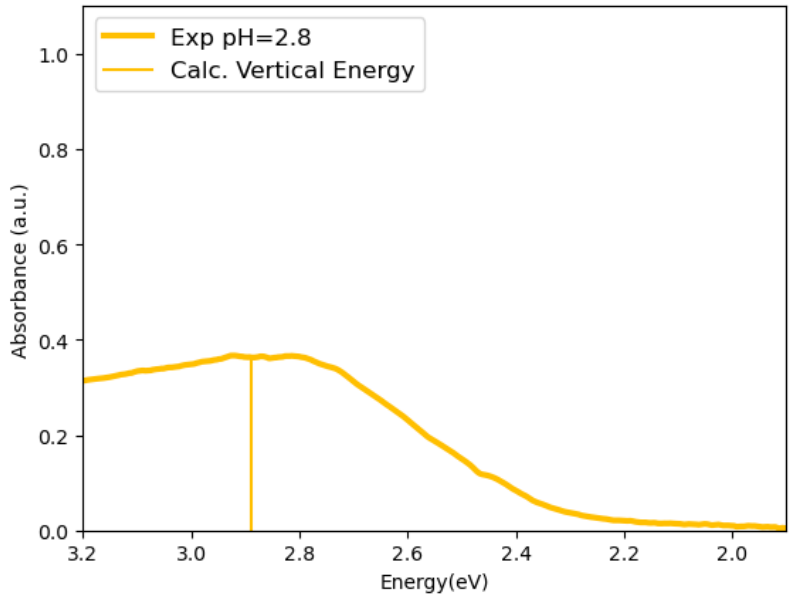
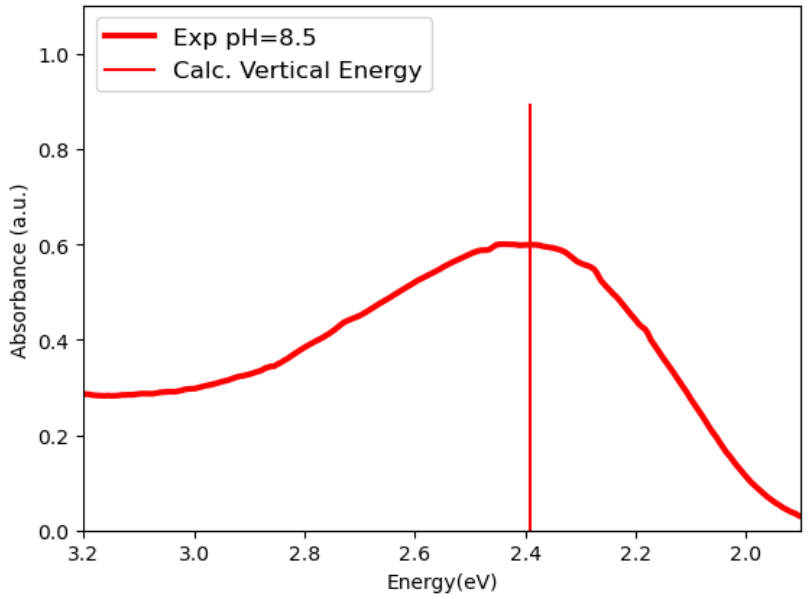
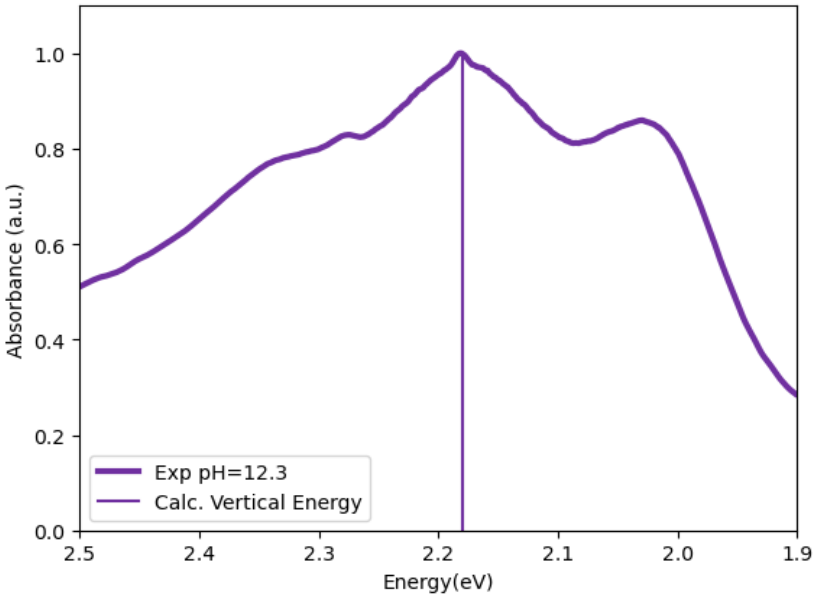


pH=12.3

A^{2-}







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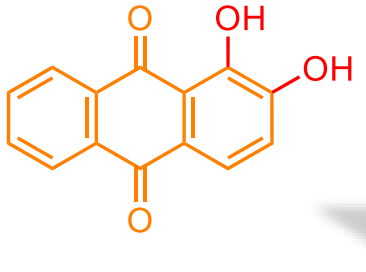
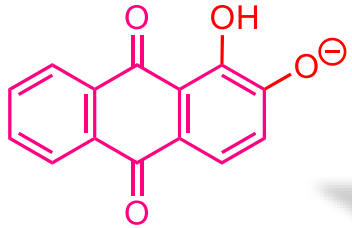
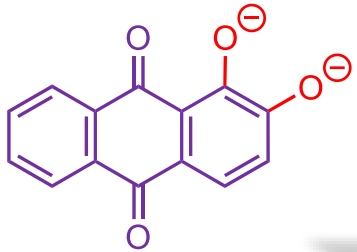
pH=2.8 H_2A

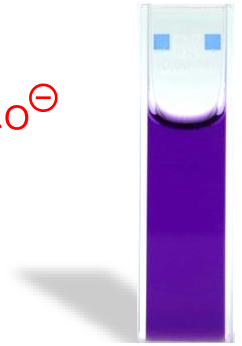


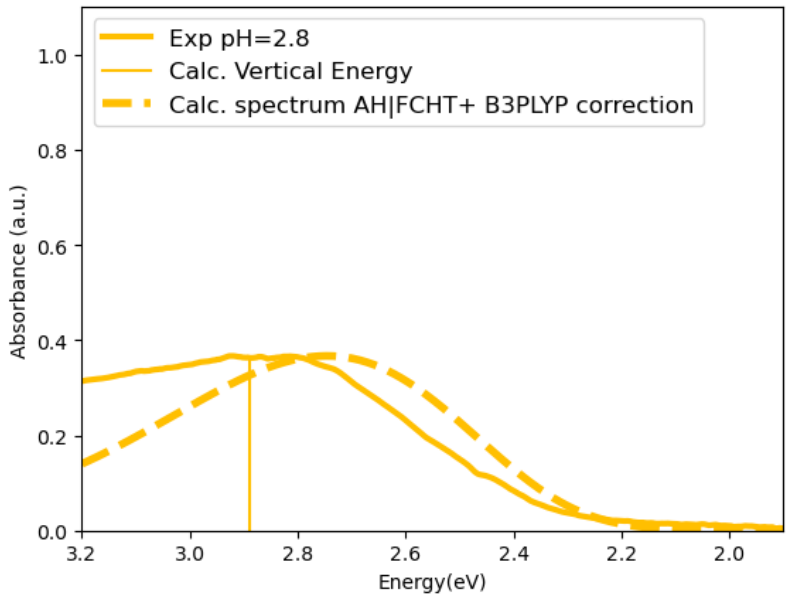
pH=8.5 HA^-

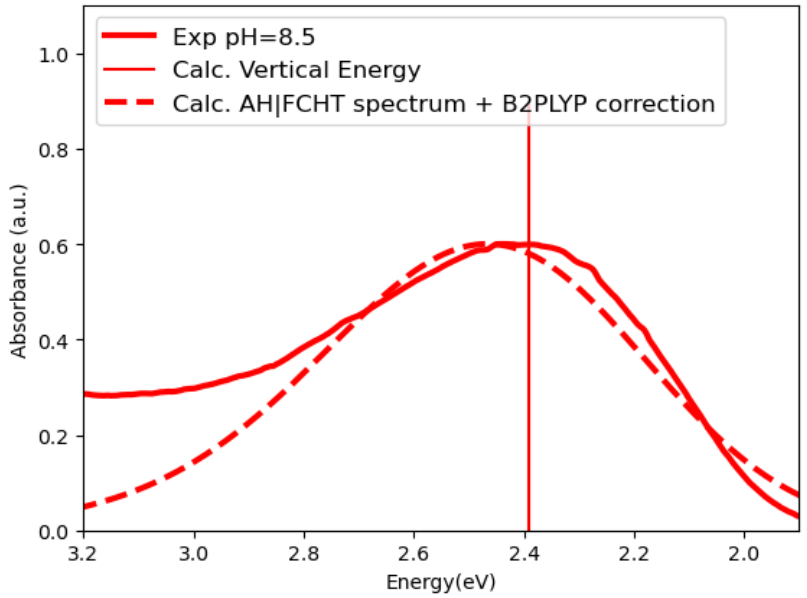


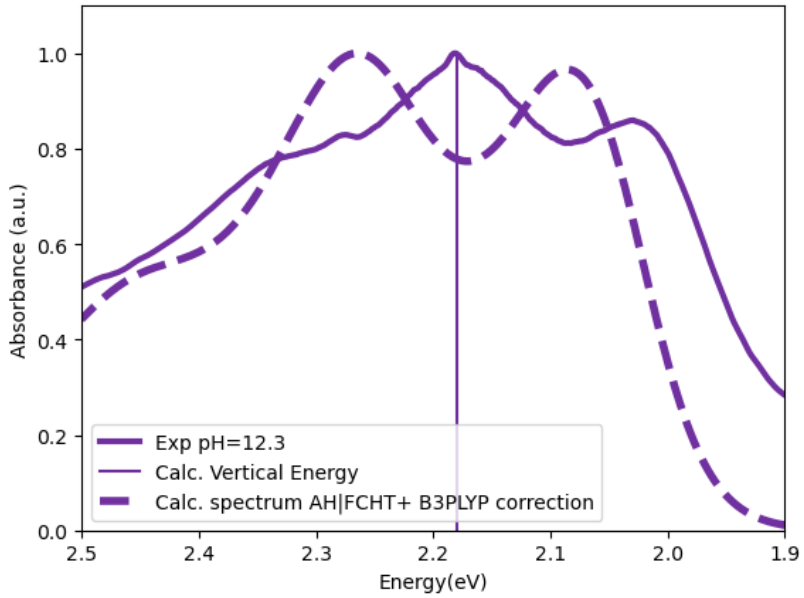
pH=12.3 A^{2-}







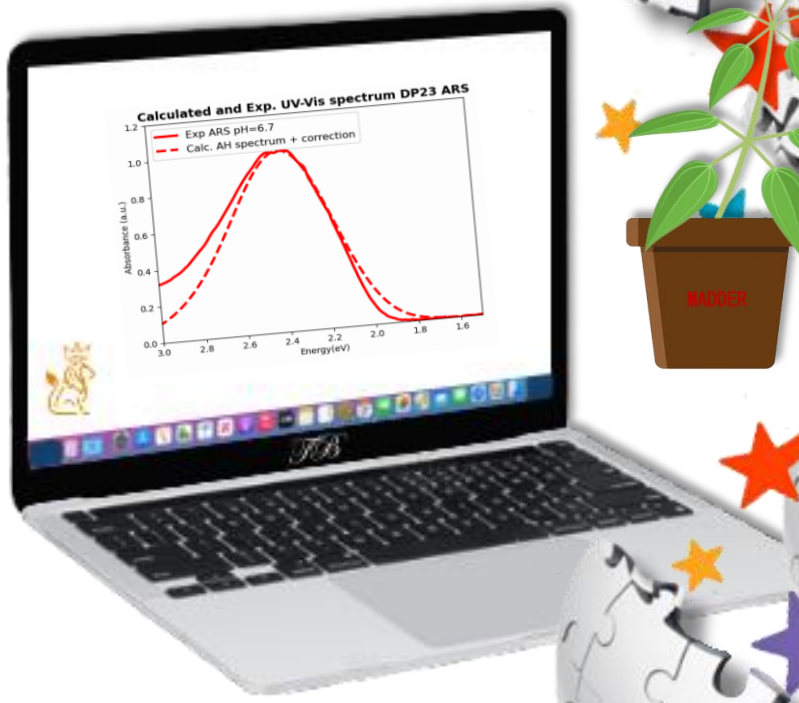




AH: Adiabatic Hessian, FC: Franck-Condon HT: Herzberg-Teller, Correction: B3PLYP

Conclusion

Use computational chemistry to unveil the secrets of photodegradation



SORBONNE UNIVERSITÉ

DECODING NATURAL DYES:

UNVEILING MADDER'S SECRET THROUGH COMPUTATIONAL CHEMISTRY

Linh TRAN[1], Romain BERRAUD-PACHE[1], Maguy JABER[1]
[1]Molecular and Structural Archeology Laboratory (LAMS), Sorbonne University, CNRS UMR 8220, Paris, 75005, France
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INTRODUCTION

To safeguard cultural heritage artifacts, it is important to unravel the photodegradation mechanisms of dyes. Among them, Madder, is a popular natural dye, whose spectroscopic properties were historically challenging to decipher due to extraction complexities, impurities, instability, and high costs. Leveraging computational spectroscopy techniques [1,2] , we now have a novel approach to reproduce, understand and predict the spectra of previously inaccessible compounds, facilitating the progress of natural dye development.

The **goal** of this study is to:
1) Predict the UV-Vis Spectrum of dyes
2) Elucidate the photodegradation mechanism

Figure.1 *Picture of Madder plant and roots used for dying textile (left). pH influences the color of Alizarin Red S colorant in water (middle). Example of predicted spectrum (right).*

METHODS AND MATERIALS

In Madder, the two main molecules are Alizarin and Purpurin. Here, their physico-chemical properties has been studied using Density Functional Theory (DFT) [3,4]. The colours are very pH and solvent dependent. Therefore in this study, I have tested different solvation models: in vacuo, implicit water solvation (CPCM), explicit water solvent molecules combined with implicit and a semi-empirical method named GFN2/xTB [5]. All calculations are done using ORCA software version 5.0.3. [6]. after an optimization step with PBE0 functional.

The effect of the different deprotonation forms on their UV spectra were also studied using RI-B2PLYP and def2-TZVP basis set. To chose the best model, the computed excitations energies for the first singlet state of each form are compared with the in house experimental data.

The photodegradation of Alizarin Red S have been studied experimentally by exposing them to different lamps (Xenon, and different LED lights) for 48h. The degradation is characterized by UV-Vis spectra.

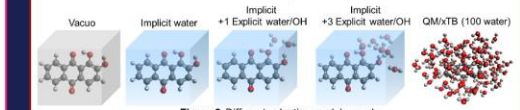


Figure.2 *Different solvation models used*

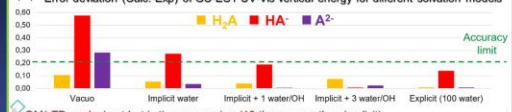
RESULTS AND DISCUSSION

ALIZARIN RED S UV-VIS SPECTRUM

Experimental UV-Vis spectra for different pH in water

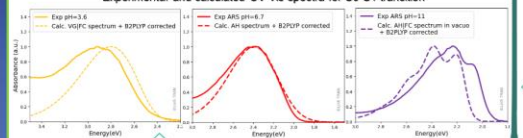
Computed energies of deprotonated forms

Error deviation (Calc.-Exp) of GS-ES1 UV-Vis vertical energy for different solvation models



-QM/xTB works best but is time-expensive (10 times more than implicit)
-Explicit water offers a good compromise
-Implicit can be used for molecules that don't interact with the solvent, like the neutral forms

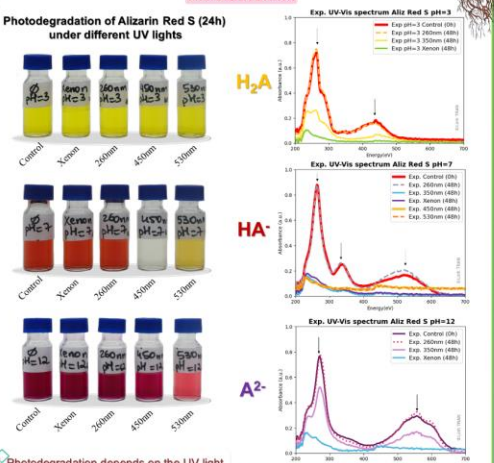
Experimental and calculated UV-Vis spectra for S0-S1 transition



Good agreement with experimental data

PHOTODEGRADATION

Photodegradation of Alizarin Red S (24h) under different UV lights



Photodegradation depends on the UV light spectrum and the pH. At lower pH, the Alizarin Red S solution is more resistant to fading than at higher pH.

The xenon lamp degrade Alizarine Red S solution for all pH after 48h. But the 260nm LED does not lead to photodegradation

CONCLUSION & PERSPECTIVES

We have concluded that the choice of the solvation model depends on the interaction of the molecules with the solvent (for example: hydrogen bonds, electrostatic interactions). When the molecules exhibit solvent interaction, the QM/xTB model has proved to be the most suitable. On the other hand, for non-interacting species like the neutral forms, an implicit solvation model is sufficient. Remarkably, the computed UV spectra together with the best solvation model show good agreement with experimental data.

Furthermore, this computational approach have demonstrated its capability to accurately predict vertical energies for other madder molecules which are not experimentaly accessible. This theoretical framework can be extended to calculate other properties such as Raman, NMR, and fluorescence, and reach a complete comprehension of the molecules [8]. Futur investigations will focus on the formation of pigments and their impact on color degradation [9]. The photodegradation depends on the UV lamps and the pH. But other factors can also impact the photodegradation [10].

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Designed by Linh TRAN, on October 2023

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