Deciphering the Secrets of Madder Molecules through Computational Chemistry

TRAN Thanh Huyen Linh;[A] **BERRAUD-PACHE Romain**;[A] **JABER Maguy** [A]

A) Laboratoire d'Archéologie Moléculaire et Structurale (LAMS), Sorbonne Université, CNRS UMR 8220, Paris, 75005, France

romain.berraud-pache@sorbonne-universite.fr

The captivating diversity and remarkable color properties of natural dyes molecules have long fascinated researchers. Madder is a plant known for being one of the main sources of natural red colorant. From its roots, more than 40 molecules from the anthraquinone family can be extracted with alizarin and purpurin being the most important ones.[1]

In our group, we used non-invasive spectroscopic techniques to measure some well-resolved UV-Vis, IR, or XAS spectra. Despite these complex methods, many data or chemical behavior cannot be obtained. In fact, several Madder dyes are not chemically stable when extracted from the roots and may not be found in the final objects. Furthermore, some of these dyes are more prone to photochemical degradation, resulting in color fading.[2]

To study these colored molecules, we have designed a reliable computational protocol which gives access to the most stable form and its related spectroscopic properties. We have first selected the most present colorant in madder, alizarin, as well as a more water-soluble analog, alizarin red S, and computed their spectroscopic properties, notably UV-Vis and NMR spectra. Our protocol enables us to characterize the impact of the solvent, *i.e.* water at different pH and its impact on the properties. We have also computed the color of the molecule according to the CIELAB framework and compared it to experimental measurements (see Figure 1).[3] Finally, this protocol has been applied to most of the colored molecules found in madder in order to create in the future an extensive open-data database.

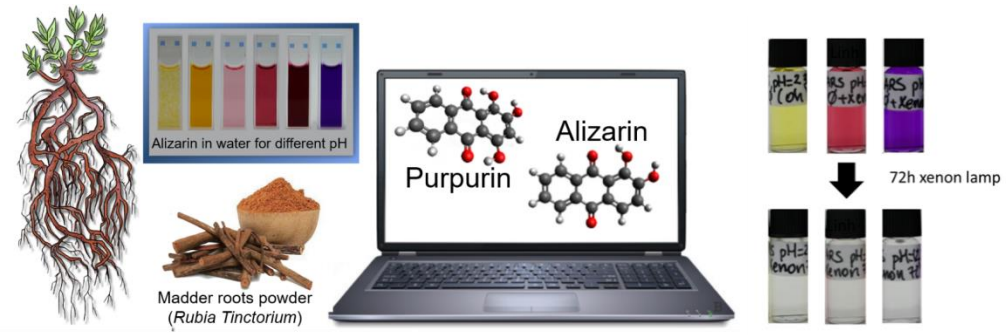

Figure 1. Representation of madder roots (left), alizarin and purpurin molecules (middle), and the color loss after light illumation (right).

Keywords: *Computational spectroscopy, cultural heritage, dye, DFT*

[1] Chavanne, C.; Troalen, L. G.; Fronty, I. B.; Buleon, P.;. *Anal Chem* **2022,** *94* (21), 7674-7682.
[2] Miliani, C.; Monico, L.; Melo, M. J.; Fantacci, S.; Angelin, E. M.; Romani, A.; Janssens, K., *Angew Chem Int Ed Engl 57* (2018), 7324-7334
[3] Tran, T. H. L.; Rigaud, B.; Jaber, M.; Berraud-Pache, R., Rapid and Complete Prediction of Alizarin in Solution by Combining Experimental Data with Computational Methods. *Dyes and Pigments* **2024,** accepted