Exploring natural's dyes color and properties through DFT and TD-DFT

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ABSTRACT

Dyes play an important role in industries such as food, medicine, textile, painting and other industries, which make life more colorful. With the rising demand of environmental protection and safeguard of people's health and safety, the development of natural dyes becomes more and more attractive. Among them, one of the most fascinating dye is Madder. Madder is an ancient dyestuff, extracted from the root of the madder plant, which grows in many countries around the world. The principal colorants in madder are alizarin and purpurin. Prior to the advent of computational chemistry, even though researchers worked diligently, deciphering the experimental spectroscopic properties of Madder's colorants posed a persistent challenge. This was primarily due to the extraction difficulty, impurities, the instability of some compounds, and their high price. Now, we can overcome this challenge with a new approach. Thanks to the application of computational spectroscopy techniques, we can reproduce, understand and predict the spectra of compounds that were previously unknown or inaccessible experimentally. [1,2]

In this investigation, we have predicted color and properties of Madder at the Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) level. We have designed a computational workflow to predict their UV-Vis and NMR spectra. Nevertheless, their spectroscopic properties are influenced by external factors like pH, solvent effects, or metallic cations. We have focused on the impact of solvation models such as implicit, explicit, or multilevel techniques (Quantum Mechanic/Molecular Mechanic QM/MM). We have also considered the possible deprotonated forms and tautomer of the dyes for different pH. The workflow has been validated for Alizarin and Alizarin red S, and extended to other molecules inaccessible experimentally. Our analysis emphasizes the importance of considering the solute-solvent interactions to reproduce the experimental measurements. This investigation will help gain insight into the correlation between structural properties with functional performance. Thanks to that, it can empower researchers to enhance natural dye's performance.

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).

References

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[2] Blackburn RS. Natural dyes in madder (*Rubia* spp.) and their extraction and analysis in historical textiles. *Coloration Technol* **2017** ;133 :449–62.