Predicting the color of natural dyes using quantum mechanics, statistical physics, and high-performance computing

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Food and pharmaceutical industries are facing a growing demand for natural pigments from consumers and law makers, as many extensively used colorants are currently under scrutiny for toxicity and carcinogenicity. In this talk we report on the results of a MAX pilot project for industrial research, carried out in collaboration with a major multinational food manufacturer, aimed at identifying optimal natural substitutes for artificial dies in the blue range.

Anthocyanins are among the most abundant natural pigments, which, depending on the chemical environment (such as acidity and copigmentation), give rise to a variety of colors and shades in the red-purple-blue gamut. In spite of the ubiquity and potential applications of anthocyanins, the mechanisms underlying their exceptional photophysical versatility are not yet fully understood.

In this work we introduce a new multiscale modeling protocol to study the optical properties of complex molecular species in solution and apply it to the photochemistry of anthocyanins in a broad pH range (1-9). Our protocol is based on enhanced sampling from classical force-fields based molecular dynamics (MD), advanced statistical analysis to identify the relevant molecular conformers, ab-initio MD to accurately sample thermal fluctuations within individual conformers, and time-dependent density-functional theory to compute absorption spectra on selected molecular frames.

Our simulations reveal that the broad range of colors expressed by anthocyanins crucially depend on the modulation of the electronic conjugation, as determined by either thermal fluctuations or molecular distortions. This finding allowed us to rationalize the chromatic behaviour of anthocyanins in terms of bond-order modulation between the aromatic moieties of the chromophore, thus enabling our industrial partners to undertake new routes towards healthier food additives, that had remained thus far unexplored.