

Abstract Submitted  
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**Solvation and thermal effects on the optical properties of natural dyes: a case study on the flavylum cyanin** ARRIGO CALZOLARI, CNR-IOM, BARIS MALCIOGLU, SISSA, Trieste IT, RALPH GEBAUER, ICTP, Trieste, IT, DANIELE VARSANO, Univ. “La Sapienza,” Rome IT, STEFANO BARONI, SISSA, Trieste IT — We present a first-principles study of the effects of both hydration and thermal dynamics on the optical properties of a natural anthocyanin dye, namely, *cyanin* (Cya), in aqueous solution. We combine Car-Parrinello molecular dynamics and time-dependent density functional theory (TDDFT) [1] approaches to simulate the time evolution of UV-vis spectrum of the hydrated Cya molecule at room temperature [2,3]. The spectrum of the dye calculated in the gas phase [4] is characterized by two peaks in the red and in the blue, which would bring about a greenish hue incompatible with the dark purple coloration observed in nature. Describing the effect of the water solvent through a polarizable continuum model does not modify qualitatively the resulting picture. An explicit simulation of both solvent and thermal effects using ab-initio molecular dynamics results instead in a spectrum that is compatible with the observed coloration. This result is analyzed in terms of the spectroscopic effects of molecular distortions, induced by thermal fluctuations. [1] *turbo*-TDDFT, B. Walker, A. Saitta, R. Gebauer, S. Baroni, *Phys. Rev. Lett.* **2006**, 96, 113001. [2] A. Calzolari, et. al, *J. Chem. Phys.* **132**, 114304 (2010). [3] O.B. Malcioglu, A. Calzolari, R. Ghebauer, D. Varsano, and S. Baroni, preprint (2010). [4] A. Calzolari, et al, *J. Phys. Chem. A* **113** 8801 (2009).

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