Submitted: 08 May 2016
Accepted: 04 August 2016
Published Online: 22 August 2016

Hydration effects on the electronic properties of eumelanin building blocks

J. Chem. Phys. **145**, 084501 (2016); https://doi.org/10.1063/1.4961147

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ABSTRACT

Theoretical results for the electronic properties of eumelanin building blocks in the gas phase and water are presented. The building blocks presently investigated include the monomeric species DHI (5,6-dihydroxyindole) or hydroquinone (HQ), DHICA (5,6-dihydroxyindole-2-carboxylic acid), indolequinone (IQ), quinone methide (MQ), two covalently bonded dimers [HM ≡ HQ + MQ and IM ≡ IQ + MQ], and two tetramers [HMIM ≡ HQ + IM, IMIM ≡ IM + IM]. The electronic properties in water were determined by carrying out sequential Monte Carlo/time dependent density functional theory calculations. The results illustrate the role played by hydrogen bonding and electrostatic interactions in the electronic properties of eumelanin building blocks in a polar environment. In water, the dipole moments of monomeric species are significantly increased ([54–79]%) relative to their gas phase values. Recently, it has been proposed that the observed enhancement of the higher-energy absorption intensity in eumelanin can be explained by excitonic coupling among eumelanin protomolecules [C.-T. Chen *et al.*, Nat. Commun. **5**, 3859 (2014)]. Here, we are providing evidence that for DHICA, IQ, and HMIM, the electronic absorption toward the higher-energy end of the spectrum ([180–220] nm) is enhanced by long-range Coulombic interactions with the water environment. It was verified that by superposing the absorption spectra of different eumelanin building blocks corresponding to the monomers, dimers, and tetramers in liquid water, the behaviour of the experimental spectrum, which is characterised by a nearly monotonic decay from the ultraviolet to the infrared, is qualitatively reproduced. This result is in keeping with a "chemical disorder model," where the broadband absorption of eumelanin

with the monomeric and oligomeric building blocks.

Acknowledgments

This work was partially supported by CNPq, CAPES, FAPEG, FAPESP, INCT-FCx, and BioMol (BRAZIL).

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