Patrizia Borghetti, Degree Thesis

Electronic properties of thin films of eumelanin

Abstract

The melanins are an important class of pigmentary macromolecule found throughout the biosphere and eumelanin is the predominant form in humans, acting as the primary photoprotectant in our skin and eyes. Unique amongst bio-macromolecules, melanins exhibit broad band absorbance in the UV and visible, conduct electricity in the condensed-phase and photoconduct; for this reason, melanins have recently attacted interest as potential materials for organic solar cells and other novel electronic devices.

Despite extensive experimental and theoretical studies conducted on both natural and synthetic melanins (and eumelanin in particular), the structure, composition and aggregation behaviour of these systems are not well understood. It is fairly accepted that eumelanins are macromolecules of the various redox forms of 5,6-dihydroxyinolequinone (DHI o HQ) and 5,6-dihydroxyindole 2-carboxylic acid (DHICA), but major questions still remain concerning their basic structural unit. Moreover, little information exists concerning their electronic structure and the time scales for the photophysical and photochemical process that follow electronic excitation in monomers.

In this thesis, electronic excitations of condensed phase eumelanin aggregates are investigated with soft X-ray spectroscopies and data are compared to *ab initio* density-functional calculations of the structural and electronic properties of isolated monomers performed by R. Gebauer (ITCP, Trieste) [1, 2]. Thin layers of synthetic eumelanins have been prepared by drop casting a solution of melanin powder in DMSO (or water) on different substrates. Film thickness and surface morphology have been characterised by Atomic Force Microscopy (AFM), which shows that eumelanin in DMSO and deposited on ITO provides quite homogeneous films. Experimental Raman spectra have been compared to that obtained from a weighted mix of the three monomers theoretical Raman spectra, revealing that HQ monomers prevail in the eumelanin aggregates, a conclusion supported by XPS data as well.

By using photoemission spectroscopies and X-ray absorption spectroscopy, we have been able to single out many spectral features in both the valence and conduction band. A comparison to *ab initio* calculations of the electronic structure of single monomers shows to which extent the calculated electronic structure catches the main features of solid state aggregates and reveals that polymerization and disorder effects, that are an intrinsic property of the eumelanin condensed phase, broaden the spectral features in the lowBE region.
Furthermore, polarisation angle dependant NEXAFS proved that eumelanin films are predominantly ordered in a configuration of tilted moleculaer planes, even though the extent of self-assembling depends on the substrate.
Finally, through RESPES at the C 1s threshold, we have been able to observed that, for the sample deposited on a polycrystalline copper substrate, a prompt delocalization of the electrons excited in the empty states occurs when electrons are excited above the π^* empty orbitals and a lower limit value of 1.6 fs have been estimated for the lifetime of these excited C 1s-π^* states.

References

[1] L. Sangaletti, S. Pagliara, P. Vilmercati, C. Castellarin-Cudia, P. Borghetti, P. Galinetto, R. Gebauer, and A. Goldoni, J. Phys. Chem. B **111**, 5372 (2007).

[2] L. Sangaletti, S. Pagliara, P. Vilmercati, C. Castellarin-Cudia, P. Borghetti, R. Gebauer, and A. Goldoni, ELETTRA Highlights **2006**, 87 .