The Melanins – A Class of Bio-organic Conductor

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Abstract

The melanins are an important class of pigmented macromolecule found throughout nature. Eumelanin is the predominant form in humans, and acts as our primary photoprotectant. The structure-property-function relationships that dictate the behavior of these biomaterials are still poorly understood. In particular, major questions still remain concerning the basic structural unit. It is well accepted that eumelanins are macromolecules of indolequinones. However, it is still a matter of debate as to whether eumelanin is actually a hetero-polymer, or composed of oligomers condensed into nano-aggregates. This is a key issue, and is the starting point for the construction of consistent structure-property-function relationships. The answer to this question also has profound implications for our understanding of the condensed phase properties of melanins. In 1974, McGinness et al.\textsuperscript{[1]} showed that eumelanin could behave as an amorphous electrical switch. They postulated that these materials may be disordered organic semiconductors. Several studies since have claimed to show the same effects, however it is by no means certain that the conductivity regime is electronic in nature. A clear idea of the basic structural unit is fundamental to developing a consistent model for condensed phase charge transport in such disordered organic systems. In my paper I will describe our group’s attempts to shed light on some of these issues. I will present results from detailed spectroscopic and solid state studies. This work is part of a wider program of theoretical and experimental research whose goal is to unravel the detailed structure-property-function relationships of these mysterious biological conductors.

1. Introduction

Eumelanin is a bio-macromolecule formed in nature by the enzymatic oxidation of tyrosine\textsuperscript{[2]}. It is a dark black pigment, with monotonous broad band absorption in the UV, visible and near IR\textsuperscript{[3]}. This property, coupled with an inherent ability to dissipate absorbed photon energy non-radiatively, is at the heart of eumelanin’s photoprotective function in the human body. The macromolecule is also chemically and photochemically very stable, and is a potent free radical scavenger and anti-oxidant\textsuperscript{[2]}.

In 1974, McGinness et al.\textsuperscript{[1]} showed that a solid pellet of eumelanin (the material is normally a powder when extracted from pigment containing tissues or when synthesized chemically) could conduct electricity. At applied electric fields of \(\sim 350\text{V/cm}\), the material was observed to switch between “low”\textsuperscript{[\(\sim 10^{-2}\text{S/cm}\)]} and “high”\textsuperscript{[\(10^{2}\text{S/cm}\)]} conducting states. This behavior led the authors to postulate that eumelanin was acting as an amorphous semiconductor – a hypothesis originally advanced in a landmark theoretical paper by Longuet-Higgins in 1960\textsuperscript{[4]}. The amorphous semiconductor model of eumelanin is now relatively widely accepted. A number of experimental studies have claimed not only to confirm this viewpoint, but also to derive band gaps, activation energies, carrier types and densities, etc. using DC and AC conductivity measurements, thermopower, photocurrentivity and optical absorption in combination with standard Mott-Davies theory\textsuperscript{[5, 6]}. What is worrying about many of these studies, is the lack of any serious consideration of the effect of adsorbed water – as demonstrated by Istražbeška et al., eumelanin conductivity is highly dependent upon atmospheric relative humidity\textsuperscript{[7]}. The latter authors also claim to show some temperature dependence of the conductivity (\(\sigma\)), but only make measurements over a very limited range (290K to 340K in-vacuum). They go on to fit the data using the standard thermally activated semiconductor model (equation 1), and extract an activation energy (\(E_a\)). This is clearly inadequate – normally, one requires at least two to three orders of magnitude in temperature before drawing such conclusions.

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\sigma = \sigma_0 \exp\left(-\frac{\Delta E_a}{kT}\right)
\]

A general model for electrical conductivity in condensed phase eumelanin remains elusive. Decoupling the effect of adsorbed water requires high vacuum, and to extract any meaningful information from DC conductivity data requires measurements over several orders of magnitude in temperature.

The mechanism of charge transport in these systems is only one question in many that are yet to be answered concerning the fundamental mesoscopic physics of melanins. In a broader sense, the basic structure-property-function relationships are still poorly understood. Critically, we do not even fully understand the nature of the basic structural unit. For the past 50 years, scientists have considered eumelanins to be large hetero-polymers of \(5,6\text{-dihydroxyindole}\) (DHI) and \(5,6\text{-dihydroxyindole, 2-carboxylic acid}\) (DHICA) (Fig.1). This hypothesis was based upon early quantum chemical considerations\textsuperscript{[4, 8]}, and on a biochemical pathway known as the Raper-Mason Scheme\textsuperscript{[9]}. However, there is a growing body of evidence (both structural and spectroscopic), that the basic unit may actually be a small (5 or 6 unit) oligomer\textsuperscript{[10]}.

Fig.1a 5,6-dihydroxyindole Fig.1b 5,6- dihydroxyindole, 2-carboxylic acid

Clearly, establishing the fundamental unit of structure in these systems is the starting point for any subsequent mesoscopic models to explain properties such as broad band absorption and electrical conductivity. We have embarked upon a comprehensive experimental and theoretical study aimed at constructing consistent structure-property-function relationships for eumelanins. Our work is motivated by the desire to better understand melanin bio-functionality (especially in relation to skin cancer), and by a fundamental interest in the condensed matter physics of disordered organic materials. In this paper we present results from spectroscopic and solid state (photoconductivity and electrical conductivity) studies. Our data supports the idea that the eumelanin basic structural unit need not be a large hetero-polymer. We propose a structural theory based upon monomeric diversity and chemical disorder, which may explain the broad band absorbance of melanin and several other spectroscopic properties. Finally, from the mesoscopic perspective, we confirm that electrical conductivity in eumelanin is indeed dominated by adsorbed water.

2. Experimental

2.1 Materials: Several types of DHI eumelanin were used in these studies. Firstly, synthetic tyrosine-derived eumelanin was purchased from Sigma Aldrich and used without further purification. Secondly, synthetic eumelanin was synthesized by the chemical oxidation of dihydroxyphenylalanine (dopa) according to standard methodology\textsuperscript{[11]}. Finally, structurally continuous solid thin films of eumelanin were prepared using a novel procedure involving electropolymerisation of dopa\textsuperscript{[12]}.
2.2 Spectroscopic Studies: Absorption and photoluminescence (PL) emission studies were carried out using dilute, high pH (~10-11) aqueous solutions of synthetic eumelanin (Sigma Aldrich). PL spectra were fully corrected for re-absorption and probe beam attenuation [3]. Absorption measurements were performed using a Perkin Elmer L40 UV-visible spectrophotometer, and PL measurements using a Spex Fluoromax 3 fluorimeter.

2.4 Solid State Studies: Room temperature electrical conductivity measurements as a function of relative humidity were made using a Keithley Source Meter Unit (SMU 2400). Different relative humidities ranging from ~10% to 95% were achieved using various saturated salt solutions [7] in a pre-purged sealed measurement chamber. Photoconductivity measurements were made using the same set-up, coupled to an Oriel Solar Simulator. Conductivity measurements vs. temperature under high vacuum (10^-6 torr) were performed in an Oxford Instruments Liquid Helium Cryostat, once again using a Keithley SMU 2400. Pressed pellets and electropolymerised films of synthetic eumelanin were used in all these studies.

3. Results and Discussion

3.1 Spectroscopy: Fig.2a shows a typical set of absorption spectra for aqueous eumelanin solutions at a range of concentrations. Of particular note is the broad monotonic form of the absorption, which fits closely a single exponential (in wavelength) rising towards the UV. It is notoriously difficult to determine the molecular weight of these macromolecules, and hence not feasible to calculate a molar extinction coefficient. However, it is clear that these extremely dilute solutions have very high absorption coefficients, particularly in the UV. These spectra can be used to correct PL emission data for the effects of probe beam attenuation and emission re-absorption [3]. Fig.2b shows the corrected PL emission for a 0.0025% by weight eumelanin solution pumped at a 0.0005% by weight eumelanin solution pumped at a range of excitation energies (wavelengths) between 360 and 380 nm. The emission is characterized by a single, broad peak typically red shifted by ~100nm relative to the excitation energy (high wavelength) limit. These data strongly suggest that a range of chemically distinct species exist within the sample, and that different excitation energies selectively pump a different member of the ensemble. These findings are supported by time resolved studies, which show lifetime distributions. This interpretation of the data is consistent with an oligomeric rather than hetero-polymeric basic structural model, and has recently been lent further weight by our quantum chemical studies using first principles density functional theory techniques [13].

3.2 Solid State Studies: Fig.3a demonstrates the strong dependence of eumelanin conductivity upon relative humidity – greater than 5 orders of magnitude in 80%. Apart from suggesting that these pellets may be extremely sensitive relative humidity sensors, it confirms the dominating nature of adsorbed water. The vacuum measurements were even more conclusive. Under 10^10 torr, even below 10K, the samples were too insulating for a conventional SMU to make a meaningful measurement of current at applied voltages of <20V. Consequently, we can say that the resistance of the sample was >1GΩ, with corresponding electrical conductivities of <10^-7 cm^-1. Clearly, any electronic contribution to the conductivity (which would have been evident under these conditions), is extremely small.

Considering the data in Fig.3 in isolation, one might be led to conclude that eumelanin is essentially an insulator in the condensed solid state, and that all the conductivity was derived from ionic sources (adsorbed water). However, under white light illumination, a measurable photo-current was generated indicative of some “semiconductor-like” behavior. UV and visible light can stimulate a significant number of charge carriers – an observation that can only be reconciled with a band gap (at least of one component within the system) of less than ~3.5 eV.

4. Conclusions

Eumelanin displays broad band UV and visible absorption, and its PL emission is characterized by a single broad feature. Additionally, the emission shows a strong dependence upon pump energy – a fact that is consistent with the stimulation of different chemically distinct species within a single ensemble. Quantum chemical calculations [13] suggest that small modifications to the monomer can lead to significant HOMO-LUMO gap changes. Hence, we propose a structural model where monomer diversity and chemical disorder are responsible for the broad band absorption and excitation energy dependent emission. This view is consistent with an oligomeric rather than hetero-polymeric basic structural unit. From a mesoscopic perspective, it appears as though the electronic contribution to conductivity is dominated by the ionic contribution from adsorbed water. The material does possess a “semiconductor-like” character, and the major challenge is now to construct a hybrid model to explain transport.

Acknowledgments

The work was funded by the Australian Research Council.

References