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Abstract

Melanin plays a crucial role as a pigment all through the animal kingdom. Being a macromolecule just on the divide between an ordered crystalline or a purely amorphous form melanin has proven a challenge to structure-function analysis. Melanin assembles from small molecules much like a jigsaw and much like in a jigsaw the fine network of interlinked measurements of excitation and emission to identify 'natural sunscreen'), provides a highly detailed fingerprint of melanin's fluorescence. A chemist’s view of melanogenesis. Tracking joined characteristic parameters during the formation process of melanin allows to identify specific sites where the absorption generates significant fluorescence emission. Some of these areas show a transient character suggesting that fluorescent structures are later transformed or integrated into non-fluorescent parts of the molecule.

1. Emulating Nature:
Making Melanin in the Lab
In the human body eumelanin derives from the amino acid Tyrosine which is then converted by enzymatic action and oxidation into the molecule L-Dopa to start the melanin formation pathway. Starting the reaction directly from L-Dopa has proven to be a realistic method to investigate melanin in laboratory conditions [1].

2. A finely balanced System:
Eumelanin derived from L-Dopa
The formation of melanin can be easily tracked by recording the evolution of its characteristic absorption spectrum. Taking absorbance scans over time reveals several isosbestic points in the spectrum. While an isosbestic point is not in itself an indication of the conversion of one species to another, it is an indication of the conversion of one species into another or of an equilibrium between two species it does show that the stoichiometry (the relative quantity of reactants and products) remains constant.

3. Joining Parameters:
Excitation-Emission Matrices (EEM)
A photo-active molecule like melanin can be characterized through a wide range of parameters: its absorbance (key to its purpose as our 'natural sunscreen'), its fluorescence (small but not at all negligible), its excitation; the size of its particles, its conductivity and many more.

With the melanin absorption spectra showing several isosbestic points we have clear indication of a highly ordered, highly interlinked formation network [2]. A small change in an external parameter – here the pH – is sufficient to blur one isosbestic point (Figure) indicating a change in the chemical composition.

Using EEMs we identify differences between lab generated and naturally occurring melanin. The addition of micro-nutrients like transition metal ions to the reaction can alter the characteristics of the melanin generated [5] (Figure below).

5. Tracking Pieces of the Puzzle:
Characteristic Lifetimes in the EEM

Excellent work has been done to characterize single building blocks of melanin [3,4]. We can use these characterisations to identify components of melanin present during the formation process. Tracking the fluorescence lifetimes in Region 'E' reveals three characteristic decay times, two showing a transient nature and a third component remaining over the course of melanin formation. The component with the lifetime of 1.79 ns is likely to be 5,6-Dihydroyindole (DHICA) [3].

6. Closer to Nature:
Influence of Effectors on Melanin Structure

The production of eumelanin in the lab is a well established technique yielding highly reproducible results. Alas melanin extracted from natural sources does show small but intriguing differences to lab generated melanin. The addition of micro-nutrients like transition metal ions to the reaction can alter the characteristics of the melanin generated [5] (Figure below).

Conclusions & Outlook

Melanin offers great opportunities as a bio-engineering tool to build bio-circuitry or as an immuno-neutral cover for implants or nano-medical compounds. To fully exploit these opportunities we need greater understanding of melanin formation. Tracking joined characteristic parameters during the formation process of complex macromolecules opens opportunities to identify and trace separate building blocks of the molecule.