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The Importance of the Fact that Melanin is Black

The biological pigment melanin is generally considered to act as a screen for biologically active quanta. Commoner & Fernberg (1961) have also postulated that melanin (a powerful electron acceptor [Pullman & Pullman, 1963]) might act as a sink for free radical species. In particular, Cotzias, Papavasiliou, Van Woert & Sakamoto (1964) hypothesized that the latter function might be relevant to the ability of such free-radical forming agents such as chlorpromazine or transition-series metals to induce dyskinetic symptoms in animal species possessing brain melanin. We would like to suggest another biological role for melanin—namely that it serves as a device by which the cell may convert the energy of excited states into heat by means of photon–phonon conversion processes.

The physical properties of melanins are probably best described in terms of amorphous semiconductor theory (McGinness, 1972), in which coupling of phonons (i.e. vibrational modes of the macromolecular structure) to electronic states plays a fundamental role. The black appearance of melanin suggests that the electron–phonon coupling in this material may be particularly efficient. An efficient phonon coupling to excited electronic states allows absorbed radiation to be partially or totally retained in the sense that the energy is transferred to the internal degrees of freedom of the macromolecule, rather than reradiating as visible or u.v. light. That is, melanin is black because absorbed light is not reradiated, but is converted to rotational and vibrational degrees of freedom (i.e. heat). Moreover, the relatively featureless spectrum of melanins from the far u.v. into the infrared (5) means that such a transition is available for any energy photon between these limits. That is, melanins are "black" over a larger range than just the visible spectrum.

Seybold & Gouterman (1965) reviewed these types of radiationless transitions in detail and pointed out that (under certain circumstances) two molecules may interact such that considerable energy is transferred, and that this exchange often occurs from thermally relaxed vibrational levels of the lowest singlet or triplet state of the (donor) molecule, whose *entire* electronic energy is transferred to the acceptor.

If melanin is the acceptor molecule the following sequence will occur: melanin accepts the energy from (say) an excited triplet state (or in the case of O_2, a singlet [Politzer, Griffen & Laseter, 1971]) leaving the donor in

the ground state and melanin in an excited state which is physically indistinguishable from the excited state produced in melanin by absorption of a photon. The energy in the excited state of melanin is then dissipated as heat in a process which is identical to that described for dissipation of energy absorbed form light.

Such considerations suggest that melanin may have a multiple role based on a single common mechanism, the electron–phonon interaction. First, as a sunscreen for biologically harmful quanta and a sink for free radicals and, secondarily, as a device for deactivating potentially disruptive electronically excited molecules.

Further, the principle of microreversability allows the latter mechanism to run in reverse. It is therefore possible that melanin might also function as a device to convert phonons into electronically active modes. Sound vibrations could increase the conductivity of melanin by increasing the mobility of localized electrons through the electron–phonon coupling (Mott, 1967).

Perhaps these roles, stemming from a common mechanism, could explain the presence of melanin pigmentation in such non-illuminated areas as the brain (Bazelon, Fenichel & Randall, 1967) and the inner ear (Erway, Hurley & Fraser, 1966).

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