Supporting Information

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SI Text

Modified Dielectric Theory. The Lorentz-Lorenz relation is given by:

$$\frac{\kappa' - 1}{\kappa' + 2} = f_{\text{melanin}} \frac{\kappa - 1}{\kappa + 2} + f_{H_2O} \frac{\kappa_{H_2O} - 1}{\kappa_{H_2O} + 2}, \qquad [S1]$$

where κ_{H_2O} is the dielectric constant of water, κ is the dielectric constant of the material in the dry state, κ' is the dielectric constant of the material in a given hydration state, f_{melanin} is the volume fraction of melanin, and f_{H_2O} is the volume fraction of water.

The best fit to Eq. **1** (main text) and Eq. **S1** is shown in Fig. 1*A* (blue line). This analysis yields an unrealistic screening length of 2.9 Å, (of the order of the size of a carbon van der Waals radius), and a dielectric constant for water of 4.9, where one would expect a dielectric constant between 40–50 (1).

Estimation of Ion Concentration as a Function of Hydration and/or pH. In principle, it is possible to calculate from first principles from a chemical equilibrium perspective the hydronium ion (proton) concentration as a function of hydration and pH (and in so doing calculate a free carrier density): However, there are significant issues with this approach which can be summarized as follows: Firstly, the different chemical ionisable sites in the melanin structure have a range of pK_as (even for the apparently identical chemical moiety); Secondly, there is a major question as to the validity of using a pK_a to calculate a dissociation fraction of a hydrated solid state sample (especially given melanins' prodigious water binding capacity). These conceptual issues manifest as follows: The K_a for a monoprotic acid is defined in terms of the activities of each species as:

$$K_a = \frac{a_{A^-} a_{H_3O^+}}{a_{HA} a_{H_2O}}.$$

Where, A represents the acid component. In this calculation it is common to assume that the water activity is unity as the reaction proceeds (i.e., in the dilute limit). Even in colloidal melanin solutions, at the reaction sites this is not a valid assumption. In our solid-state experiments where we provide water vapour to the reaction sites, this assumption is even less valid. In principle, for the comproportionation equilibrium reaction the above can be rewritten as:

$$K = \frac{a^2_{SQ^-} a^2_{H_3O^+}}{a_{HQ}\, a_Q\, a^2_{H_2O}},$$

where, SQ, Q, and HQ respectively define the semiquinone, quinone, and hydroquinone. In principle, if K and the SQ, Q, and HQ activities were known, one could calculate the hydronium ion activity (and hence derive a concentration) as a function of the theoretical pH. However, given the reservations highlighted above with respect to estimating K in the solid state, and the virtual impossibility of knowing with any accuracy the activities of SQ, Q, and HQ, any estimate of $[H_3O^+]$ is, to say the least, dubious. There is one example in the literature of the measurement (estimate) of hydrogen ion production during the electrolysis of solid state melanin samples (2) in an attempt to measure the relative concentrations of protonic and electronic conduction. However, coulometric studies have a major disadvantage in that the gases evolved may not be due to the charge carriers in the system.

In summary, it would, in principle, be possible to calculate the hydronium ion concentration by estimating the solid-state equilibrium constant, but a new methodology would be required to measure the reactant and product activities of the comproportionation reaction.

1. Löffler G, Schreiber H, Steinhauser O (1997) Calculation of the dielectric properties of a protein and its solvent: theory and case study. *J Mol Biol* 270:520–534.

2. Powell MR, Rosenberg B (1970) The nature of the charge carriers in solvated biomacromolecules. *Bioenergetics* 1:493–509.

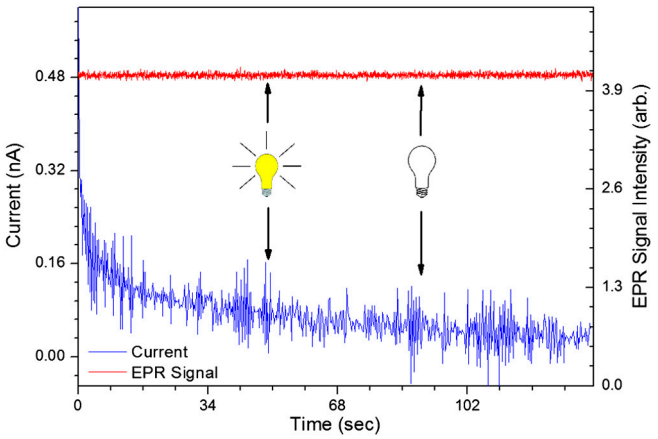

Fig. S1. Simultaneous photo-EPR (red) and photoconductivity (blue) measurements of a dry melanin pellet. Light bulbs indicate when the light was switched on and off. There is no change in the photoconductivity nor in the EPR signal.

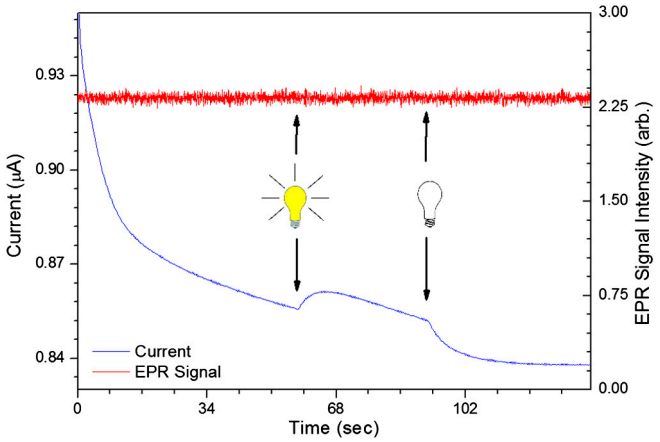

Fig. S2. Simultaneous photo-EPR (red) and photoconductivity (blue) measurements of a melanin pellet (17.2% hydration). Light bulbs indicate when the light was switched on and off. Clearly there is no change in the EPR signal while the photoconductivity is strongly modulated. This confirms that the intrinsic spin is not connected with electrical conduction in melanin.