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Study of optical properties of electropolymerized melanin films by photopyroelectric spectroscopy

Abstract Photopyroelectric (PPE) spectroscopy, in the 350–1,075 nm wavelength range, was used to study the optical properties of electropolymerized melanin films on indium tin oxide (ITO) coated glass. The PPE intensity signal as a function of the wavelength λ, $V_n(\lambda)$ and its phase $F_n(\lambda)$ were independently measured. Using the PPE signal intensity and the thermal and optical properties of the pyroelectric detector, we were able to calculate the optical absorption coefficient β of melanin in the solid-state. We believe this to be the first such measurement of its kind on this material. Additionally, we found an optical gap in these melanin films at 1.70 eV.

Keywords Melanin · Photopyroelectric spectroscopy · Optical properties

Introduction

The melanins are a class of bio-macromolecules found throughout nature (Meredith et al. 2005). In humans, they act as pigments and photoprotectants in our hair, skin and eyes. They are also found in the brain stem and inner ear, where their roles are less well defined. Eumelanins (also known as dopa-melanins), the pre-dominant form in humans, are broad band ultra-violet and visible light absorbers. Additionally, they are thought to be bio-macromolecular semi-conductors (McGinness

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et al. 1973). This combination of properties has led to the novel proposition that they may be useful, from a technological perspective, as functional "electronic soft-solids" (Meredith et al. 2005). Despite significant scientific effort over the past 30 years, large knowledge gaps concerning the basic physics and chemistry of melanins still exist. These materials are particularly intractable from the analytical perspective, since they are chemically and photochemically very stable, and virtually insoluble in most common solvents. Hence, we do not fully understand key properties such as electronic structure versus chemical composition, or why (and how) melanins conduct electricity in the condensed solid-state. Significant knowledge gaps also exist regarding melanin biofunctionality. It is well accepted that these molecules serve as our primary photoprotectants. However, the mechanisms by which melanin aggregates dissipate potentially harmful solar radiation are not well understood. It has been proposed that efficient coupling between photo-excited electrons and phonon modes allows non-radiative dissipation of absorbed photon energy—i.e., melanins can effectively turn biologically harmful photons into harmless heat (Crippa and Viappiani 1990).

Photothermal spectroscopic (PTS) techniques have been extensively and successfully applied to solid-state materials for obtaining their thermal and optical parameters (Tam and Wong 1980; Murphy and Aamodt 1981; Coufal 1984; Mandelis 1984). In these techniques, a pulsed light beam is absorbed in a solid sample and the converted heat (non-radiative conversion) diffuses into the bulk structure; the sample expansion, or the temperature gradient, is then detected by an appropriate sensor system. The detected signal depends on the optical and thermal properties of the sample: the optical absorption coefficient $\beta(\lambda)$ (λ being the light wavelength), the non-radiative conversion efficiency $\eta(\lambda)$, the thermal conductivity k, and the thermal diffusivity coefficient α. It also depends on experimental control parameters such as the chopping frequency f of the incident light beam.

Therefore, the principles of PTS techniques lie in the light-to-heat conversion efficiency of the sample structure and in the heat diffusion mechanisms across the material bulk. Several kinds of photothermal techniques have already been described in the literature, in which various physical principles have been used for detecting the photothermal signal: microphones in closed photoacoustic chambers (Tam and Wong 1980), optical detection in the Mirage effect (Murphy and Aamodt 1981), pyroelectric detection in photopyroelectric (PPE) spectroscopy (Coufal 1984; Mandelis 1984), and so on. Both the traditional photoacoustic spectroscopy (PAS) (Rosencwaig 1980) and the more recent photopyroelectric spectroscopy (PPES) have been used for studying the thermal and optical properties of polymeric films (Melo et al. 1993; de Albuquerque et al. 2000, 2002, 2003). Among the various physical parameters that can be measured, the optical absorption coefficient is important since it is unique for each material. In this current study, we used samples of electropolymerized (EP) melanins on indium tin oxide (ITO) glass. The normalized PPE intensity signal $V_n(\lambda)$ and its phase $F_n(\lambda)$ were independently measured. Equations for both the intensity and the phase of the PPE signal, taking into account the thermal and the optical characteristics of the pyroelectric detector, have been used to fit the experimental results. We believe that this is the first complete study of the optical properties of melanin in the solid-state form. This work is part of a larger endeavor whose aim is to establish the structure-property relationships in these intriguing bio-macromolecules.

Experimental

The photothermal spectrometer used in our experiments is schematically shown in Fig. 1. It comprises an optical probe (light source, monochromator, and chopper), the custom-made pyroelectric or photoacoustic chamber, and the measuring system. When the monochromator is used (in our case a Jobin Yvon HRS 2), either an optical cable can be connected to the photothermal chamber, substituting the mirror, or the chamber can be put directly into the exit slit of the monochromator. The measuring system was composed of a Stanford Research System SR 530 lock-in amplifier that was locked at the cho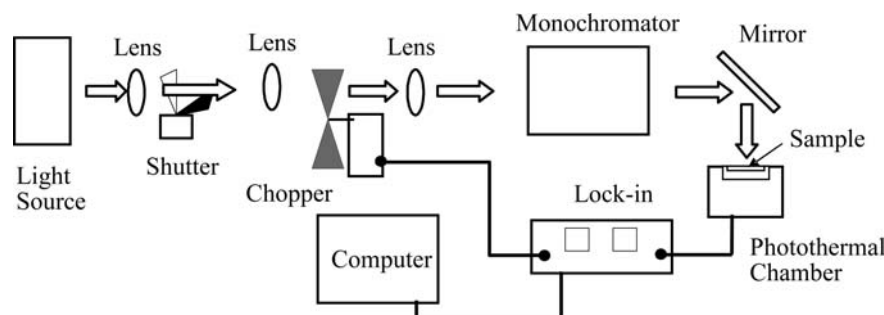pper frequency. Data were acquired automatically and the system was controlled by a computer via a GPIB interface. The mechanical slotted wheel chopper (Stanford Research System SR 540) modulated the incident light. The PPE cell was set up for the EP films using the ITO glass substrate as a window of the cell. The wavelength range was between 350 and 1,075 nm. We used long pass filters to avoid overtones of the monochromator grating (this is extremely important for $\lambda >$ 700 nm). For wavelength scanning we used a 150 W ozone free Xenon arc lamp (Thermo Oriel).

The PPE cell was set up with the window being the ITO glass substrate. The generated heat was detected by the pyroelectric detector β-poly(vinylidene difluoride) (PVDF) film, with Ni-Al electrodes evaporated on both surfaces for electrical contacts, one of which was painted with a very thin layer of black ink and was in direct contact with the sample. The thickness of this detector was 40 μm.

Sample preparation

Thin films of dihydroxyphenylalanine (DOPA)-melanin were synthesised by the oxidative electropolymerisation of DL-DOPA (Sigma–Aldrich). The initial solutions were 30 mM of DL-DOPA in sodium tetraborate buffer (Sigma–Aldrich, 0.1 M, pH 9). Electrical current was passed through the solutions by dropping up to 20 V across a copper cathode and ITO anode, using a DC power supply. To accelerate the formation of melanin, the solution was initially oxidised by mechanical stirring for 10–15 min at a voltage that generated 10–20 mA/cm^2 of current. The solution was then left in atmospheric conditions at a current density of 0.5 mA/cm^2 for 1-8 days, depending on the desired thickness of the film. During this time, the solution turned black and a soft black melanin film formed on the anode. Once the desired thickness was achieved, the films were dried slowly in a sealed container, with various saturated salt solutions to control the relative humidity. The humidity was stepped down from 94% to about 50% over a period of 3–5 days. Slow drying minimised cracking of the films. In the course of drying, the films decreased in thickness from about 100–500 to 1-2 μm for the thinnest film. We obtained samples with various thicknesses, ranging from ~1 to 65 μm. The thinnest sample was grown in 1 day of the reaction, the 25 μm one in 5 days and the thickest one in 8 days.

Fig. 1 Experimental setup of the PPES system

PPES theory

The PPE spectrometer used in our experiments is schematically shown in Fig. 1. The mechanical slotted wheel chopper modulates the incident light, giving the intensity as (Rosencwaig 1980; Melo et al. 1993; de Albuquerque et al. 2000, 2002, 2003; Mandelis and Zver 1985; Christofides 1993):

$$I = \frac{I_0}{2}[1 + \cos(\omega t)], \tag{1}$$

where I_0 is the amplitude of the beam intensity and $\omega = 2\pi f$ (f is the chopping frequency). The absorption of this modulated pulsed light gives rise to a periodic heating of the sample, owing to non-radiative relaxation of excited states.

The detected voltage signal $V(\omega, t)$ is (Melo et al. 1993; de Albuquerque et al. 2000, 2002, 2003; Mandelis and Zver 1985; Christofides 1993):

$$V(\omega, t) = \left[\frac{p}{K\varepsilon_0} \int_{L_P} T_P(\omega, x) dx \right] e^{i\omega t}, \tag{2}$$

where p is the pyroelectric coefficient of the detector, L_P is the detector thickness, $T_P(\omega, x)$ is the temperature field in the bulk of the detector, K is the relative dielectric constant of the detector, $i = (-1)^{1/2}$, and ε_o is the vacuum dielectric permittivity. The heat propagation across the whole chamber is governed by the heat diffusion equations of each medium, coupled via boundary conditions at the interfaces ($T_a = T_b$ and $k_a\, dT\, a/dx = k_b\, dT\, b/dx$, a and b representing consecutive media), as established by (Mandelis and Zver 1985). The signal $V(\omega,t)$, obtained by integrating the diffusion equations, is normalized by the ratio $V(\omega,t)/V_R$, where V_R is the signal measured directly over the detector painted with a very thin layer of a black ink. In this latter case, the detector is considered thermally thick and optically opaque in the whole wavelength region. The normalized voltage signal is then given by (Melo et al. 1993; de Albuquerque et al. 2000, 2002, 2003; Mandelis and Zver 1985; Christofides 1993):
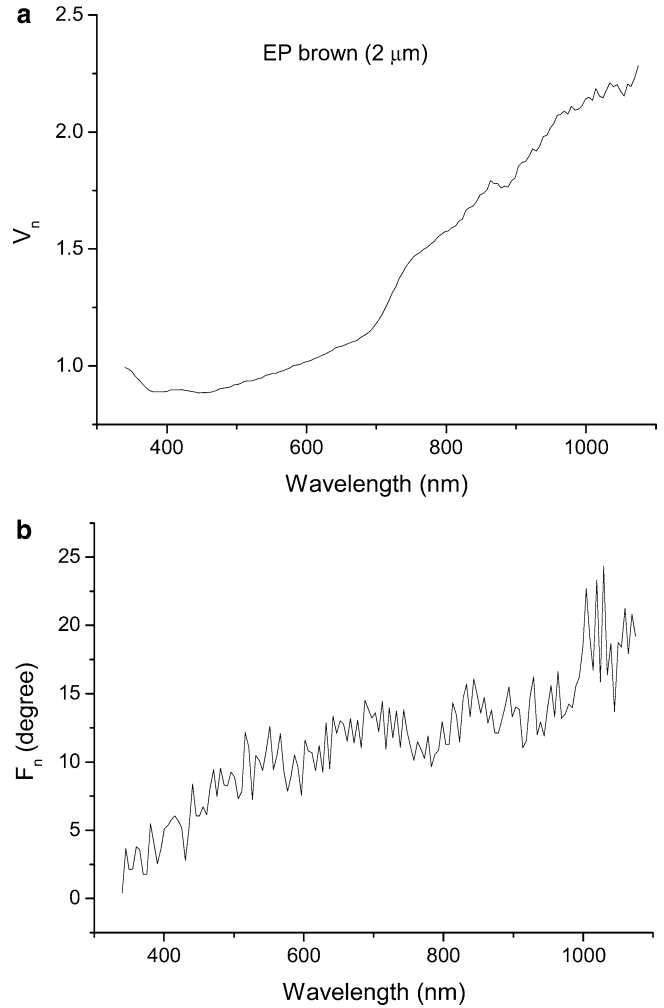

Fig. 2 PPE spectrum of the thinnest EP melanin (*brown*). **a** Voltage and **b** phase

thermal diffusivity and conductivity, for melanin pellets were obtained by using PPE spectroscopy and the data can be found in reference (de Albuquerque et al. 2005). Here we are interested in obtaining the optical absorption coefficient β. Equation 3 does not allow us to solve for β analytically and we must resort to

$$V_n(\beta_s, \omega) = \left[\begin{array}{l} \left(\frac{\eta_s r_s}{r_s^2 - 1}\right)[2(b_{gs} + r_s) - [(r_s + 1)(b_{gs} + 1)e^{\sigma_s L_s} - (r_s - 1)(b_{gs} - 1)e^{-\sigma_s L_s}]e^{-\beta_s L_s}] \\ + [(b_{gs} + 1)e^{\sigma_s L_s} - (b_{gs} - 1)e^{-\sigma_s L_s}]e^{-\beta_s L_s} \\ \times \left[\frac{b_{gs} + b_{ps}}{(b_{gs} + 1)(b_{ps} + 1)e^{\sigma_s L_s} - (b_{gs} - 1)(b_{ps} - 1)e^{-\sigma_s L_s}}\right], \end{array} \right] \tag{3}$$

where $r_j = \beta_j /\sigma_j$, $\sigma_j = (1+i)a_j$, and $a_j = (\pi f/\alpha_j)^{1/2}$ (j is a medium, g is the gas, s is the sample and p is the pyroelectric) with $b_{jm} = k_j a_j /k_m a_m$ (m is another medium). α is the thermal diffusion coefficient, k the thermal conductivity and η_S the non-radiative conversion efficiency. The thermal parameters, such as

numerical methods to isolate the optical absorption coefficient, using measured values of V_n. The non-radiative conversion efficiency $\eta_S(\lambda)$ is very near to unity because luminescence effects in melanins have a very low efficiency (less than 10^{-3}) (Meredith and Riesz 2004).

Results and discussion

Figures 2–4 shows PPE spectra at 20 Hz chopping frequency, normalized voltage and phase, of EP melanin films. These figures show transmission-like behavior for V_n and demonstrate how the saturation region of the spectra develops with the thicknesses of the samples. The normalized phase spectra obey the behavior of thermally thin films, i.e., the thermal wave generated inside the sample reaches the detector. The thinnest sample, which is brown in colour, is semi-transparent in the whole wavelength region, so that the phase develops similarly to the format of the V_n spectrum (transmission-like), i.e., smaller values of the signal for less transparent wavelengths. Any transmitted light is absorbed by the detector, thus, causing heat to be generated directly. This means that the heat generated inside the sample does not greatly affect the phase in regions of sample transparency. This heat, produced due to the absorption of light directly in the detector, is responsible for the positive phase lags in Fig. 2b. The reader should note that there are also experimental phase lags (instrumental phase variations) due non-uniformities in the black-layer thickness on the PVDF film (Christofides 1993).

For thicker samples, the normalized phase behavior was quite different because the melanin films are virtually opaque over large regions of the spectrum, i.e., there is no heat generated directly in the detector. Consequently, we observe greater phase lags and the phase spectra of Figs. 3 and 4 represents "absorption-like" behaviour. However, the real saturation of the absorption, which represents photothermal saturation here, is depicted in the V_n spectra, as shown in Fig. 4. From these figures, we can conclude that some form of optical gap starts approximately at 730 nm, as evidenced by the phase spectra in Figs. 3 and 4 and in the voltage spectrum in Fig. 4. Comparing the V_n spectra with that of single quinone molecules or quinone oligomers, which possess an absorption band at around 780 nm (Powell et al. 2004), it seems that the bands that appear at around 800 nm in these V_n spectra, explicitly in Fig. 3 and implicitly as shoulders in Figs. 2 and 4, belong to single quinone molecules or oligomers formed in the electropolymerization process. The optical gap that we
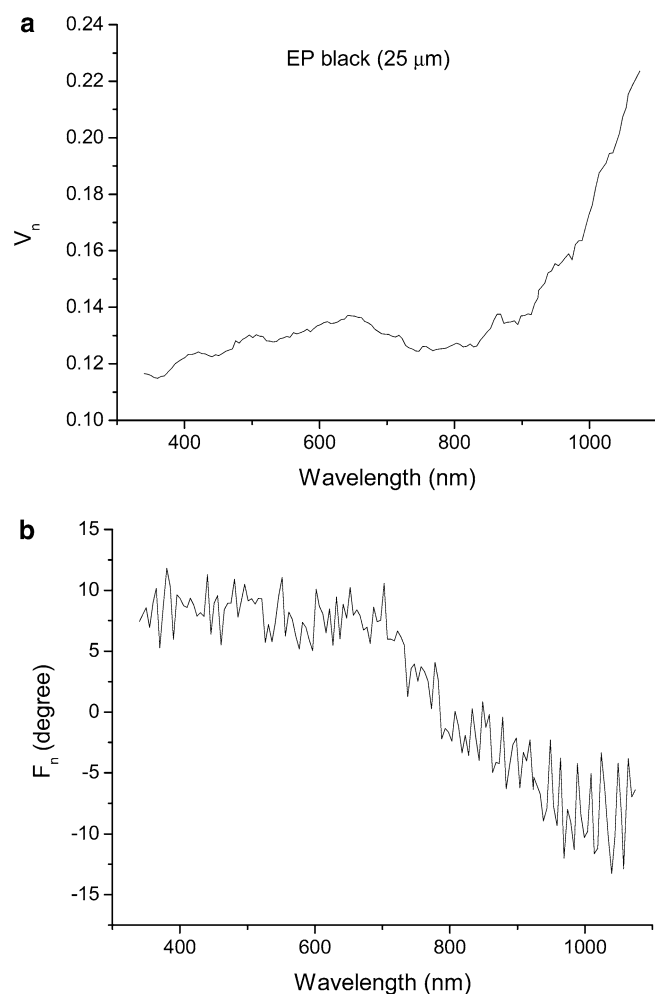

Fig. 3 PPE spectrum of 25 μm EP melanin film (*black*). **a** Voltage and **b** phase
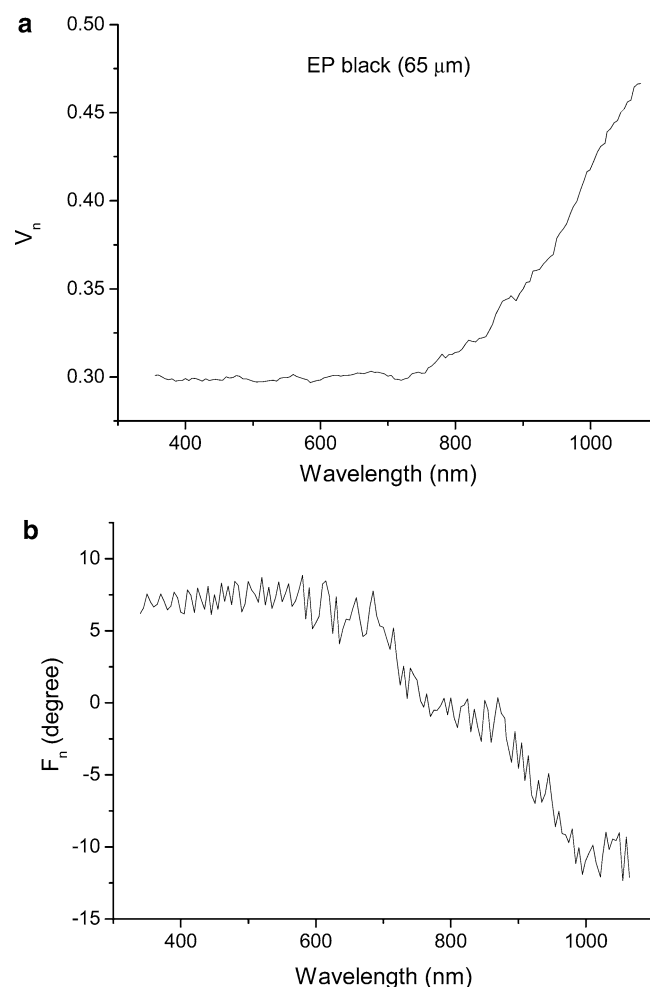

Fig. 4 PPE spectrum of the thickest (65 μm) EP melanin film (*black*). **a** Voltage and **b** phase
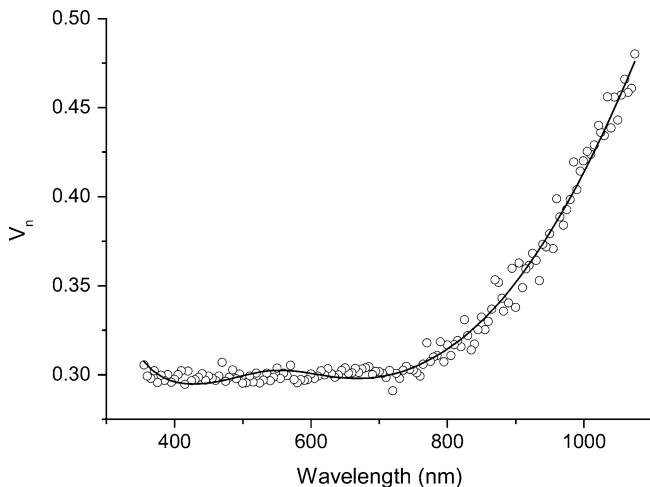
Fig. 5 PPE spectrum of the 65 μm EP melanin film with the fitting using Eq. 3

Fig. 7 The optical gap of the melanin sample using the shoulder of the spectrum for β plotted versus energy in electron-volts

observe is related to the band that saturates when the film thickness is increased.

Figure 5 shows the fitting using Eq. 3 to the V_n spectrum of Fig. 4. Since we do not know precisely how many bands exist in the wavelength region below 730 nm, as there is no data related to this in the literature as yet, we used two Gaussian curves (the minimum required), representing the optical absorption coefficient $\beta(\lambda)$, to fit the data. Currently, there is significant debate as to the origin of the optical absorption spectra in melanins and, hence, the number of bands in this region (Meredith and Riesz 2004; Powell et al. 2004). We used the thermal parameters previously obtained by us for melanin pellets (de Albuquerque et al. 2005) and unity non-radiative conversion coefficient (Meredith and Riesz 2004). We permitted the fitting routine to adjust the intensity, the line-width and the center of the Gaussian curves. We verified that the intensity of the first Gaussian curve was approximately equal to that of the β spectrum depicted in Fig. 6.
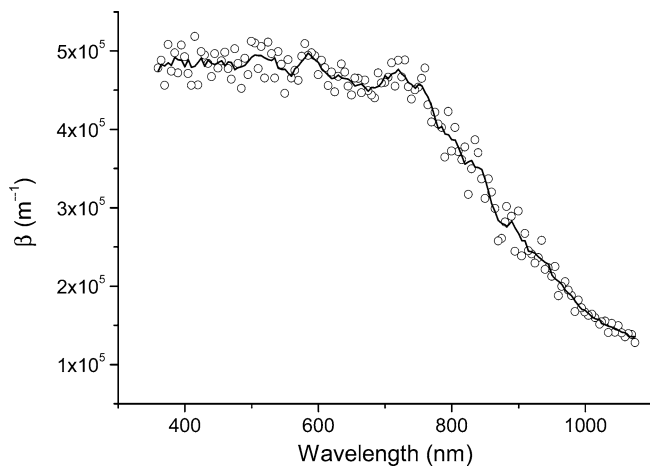

Fig. 6 Optical absorption coefficient spectrum for a melanin sample, obtained from the V_n spectrum of Fig. 4, using Eq. 3. The *line* represents a mathematical smooth of the spectrum
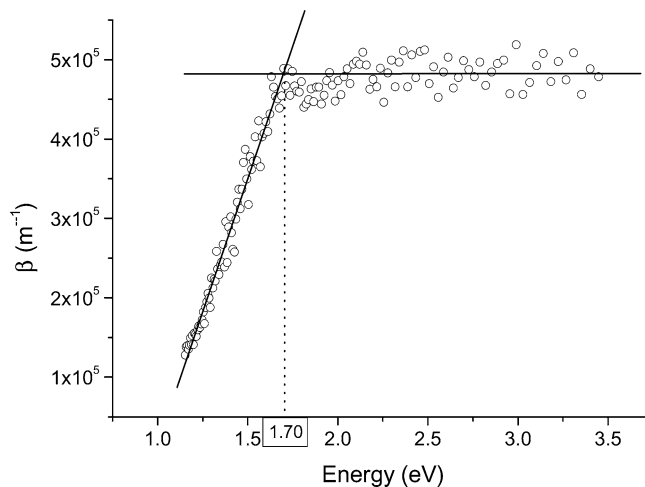
Figure 6 shows the optical absorption coefficient β obtained from the V_n spectrum of Fig. 4, using Eq. 3. We resolve this equation to obtain β numerically. The line represents a mathematical smooth of the data and is depicted only for visualization of the shoulder of the curve. According to this result, we conclude that the melanin sample is opaque, i.e., $\beta^{-1} < L_S$, in the whole wavelength region, but the signal saturates only for those wavelengths below 730 nm, which corresponds to an optical gap in this melanin sample. Figure 7 shows β plotted in energy space and the optical gap can clearly be seen at 1.70 eV. Similar spectra for the thinner samples could not be obtained because of inadequate sample thicknesses. The mathematical routine was not able to give the β numerically.

The gap that we have measured at 1.70 eV has not hitherto been observed in solid-state melanin samples. Normally, a simple optical transmission measurement can directly reveal the absorption edges. However, this is a major issue for melanin films since their aggregated structure causes significant Mie scattering. In such circumstances, one requires measurements of specular and diffuse reflectance and transmittance in order to reveal an edge (an optical gap) and calculate an absorption coefficient. As we have shown in this paper, the gap that emerges at 1.70 eV is a subtle feature—these solid-state melanin samples continue to demonstrate strong absorption into the near infra-red. Unless extremely accurate total reflectance and transmittance measurements can be made (a very difficult task for such a highly absorbing material), the Mie scattering will obscure any absorption edges and prevent the accurate calculation of absorption coefficients. Therein lies the key advantage of our photothermal technique.

Conclusions

In this paper, we have presented the application of a particular photothermal technique, PPES, to study the

optical properties of melanins. From the experimental point of view, this technique provides a powerful investigation of such properties since it produces measurable signals for completely opaque samples. Despite the complexity of the PPE equation, we were able to numerically obtain the optical absorption coefficient for electropolymerized melanin films. More importantly, our data indicates that these melanin samples possess a solid-state optical gap of 1.70 eV. This value corresponds to the minimum energy required to cause a transition between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of the system. As such, it corresponds to the HOMO-LUMO gap and is consistent with our first principles density functional theory calculations of the gap of indolequinone (Powell et al. 2004). We believe our measurements of β to be the first reported for melanin in the solid-state. Furthermore, our measurement of the optical gap (1.70 eV) confirms our earlier estimates (de Albuquerque et al. 2005). This data will undoubtedly assist in the on-going efforts being made to understand the condensed phase physics and chemistry of these important bio-materials.

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