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affiliée à l'Université de Montréal

**Eumelanin Pigment for Green Organic Electronics: Band Structure,
Nanoscale, and Magnetic Properties**

DIEUDONNÉ NIYONKURU

Département de génie physique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

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Cette thèse intitulée :

Eumelanin Pigment for Green Organic Electronics: Band Structure, Nanoscale, and Magnetic Properties

présentée par **Dieudonné NIYONKURU**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*

a été dûment acceptée par le jury d'examen constitué de :

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DEDICATION

"I do not know what I may appear to the world, but to myself, I seem to have been only like a boy playing on the seashore and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me." - Isaac Newton.

"Je ne sais pas ce que je pourrais paraître aux yeux du monde, mais pour moi, j'ai été comme un garçon jouant sur la plage et m'amusant de temps en temps en trouvant une pierre plus lisse ou un coquillage plus joli que d'ordinaire, tandis que le grand océan de la vérité s'étendait devant moi, inexploré et inconnu." - Isaac Newton

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RÉSUMÉ

Nous vivons dans une époque où les déchets d'équipements électriques et électroniques (DEEE) représentent des déchets solides dont la quantité est en croissance rapide, contribuant à la pollution environnementale. Cette thèse de doctorat s'est focalisée sur le bio-pigment « eumélanine », un candidat potentiel pour le développement d'électronique organique verte, qui vise à atténuer les problèmes liés aux DEEE. L'eumélanine présente une conductivité ionique-électronique mixte qui dépend de l'humidité, prometteuse pour les applications basées sur la transduction ionique-électronique dans les signaux biologiques et les applications de semi-conducteurs organiques. Explorer cette propriété nécessite encore des études approfondies sur les structures électroniques et morphologiques du bio-pigment. À cet égard, nous avons étudié sa structure de bandes d'énergie, ses nanostructures et ses propriétés magnétiques pour éclairer son comportement semi-conducteur.

Premièrement, nous avons localisé les plus hautes orbitales moléculaires occupées et les plus basses orbitales moléculaires non occupées (HOMO et LUMO) des couches produites à partir des monomères d'eumélanine chimiquement contrôlés (DHI et DHICA). Différentes méthodes de production de couches ont été utilisées, à savoir le revêtement par rotation de la solution et l'évaporation thermique, tout en considérant différentes atmosphères lors de la formation des couches après la déposition, (c'est-à-dire une atmosphère riche en ammoniac, une atmosphère où l'oxygène et l'humidité sont contrôlés, et une évaporation thermique sous vide). Les méthodes de photoémission inverse et directe ont montré que les emplacements des niveaux d'énergie HOMO et LUMO se situent dans les marges de 5,34-5,80 eV et 3,80-4,0 eV, respectivement par rapport au niveau du vide. Les résultats ont montré une forte dépendance de la structure des bandes d'énergie des couches d'eumélanine sur la méthode de déposition ainsi que la structure moléculaire des monomères.

Deuxièmement, nous avons utilisé la microscopie à force atomique (AFM) et l'AFM conductrice pour élucider la structure nanométrique et la réponse électrique de *Sepia* eumélanine. Les images d'AFM ont montré des granules quasi-sphériques comportant des protubérances à leur surface, avec une largeur moyenne d'environ $18,5 \pm 6,4$ nm et une hauteur moyenne d'environ $3,0 \pm 1,6$ nm. Les protubérances sont compatibles avec les sous-unités de granule considérées dans le développement hiérarchique de *Sepia* eumélanine, tel que proposé dans la littérature. L'AFM conductrice a révélé, pour la première fois, une réponse électrique à l'échelle du nanomètre des couches formulées à

partir de l'encre de *Sepia* eumélanine, indiquant un transport de porteurs de charge à travers des structures intra- et intergranulaires. Considérant les similarités entre la structure supramoléculaire des couches synthétiques de DHI/DHICA et celle du biopigment naturel à l'échelle des protubérances, les résultats liés à la structure de bandes et aux nanostructures ouvrent la voie à la définition d'interfaces eumélanine-électrode métallique appropriées pour une injection efficace de porteurs de charge et leur transport dans les couches d'eumélanine.

Enfin, nous avons proposé d'explorer par les techniques de spectroscopie de résonance paramagnétique et de magnétométrie la dépendance de l'aimantation des pastilles de *Sepia* eumélanine sur humidité afin de comprendre l'origine de sa réponse électrique au niveau moléculaire. Les résultats préliminaires sont présentés dans l'annexe A de cette thèse. Les pastilles ont montré une coexistence de comportement ferromagnétique et paramagnétique à la température ambiante, avec une aimantation qui diminue à haute humidité. Les résultats de cette thèse de doctorat fournissent des perspectives sur la relation « structurepropriété » des matériaux biosourcés, stratégiques pour le développement de l'électronique organique durable.

ABSTRACT

We live in an age where waste electrical and electronic equipment (WEEE or e-waste) is the fastest-growing solid-state stream waste, leading to environmental pollution. This PhD thesis focused on eumelanin pigment, a potential candidate for the development of organic green electronics, which aims to alleviate the e-waste issues. Eumelanin features mixed ionic-electronic conduction that depends on humidity, promising for both ion-to-electronic transduction in biological signals and semiconductor-based applications. Exploring this property still requires further studies on the electronic and morphological structures of the pigment. In this regard, we studied its band structure, nanostructure, and magnetic properties to shed light on its semiconducting behaviour.

First, we located the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of films produced from chemically controlled eumelanin building blocks (DHI and DHICA). Different film production methods were used, which are solution spin-coating and thermal evaporation (considering different atmospheres during film formation i.e. ammonia atmosphere, oxygen- and humidity-controlled atmosphere, and thermal evaporation in vacuum). The ultraviolet and inverse photoemission spectroscopy methods showed that the locations of HOMO and LUMO are in the ranges of 5.34-5.80 eV and 3.80-4.0 eV, respectively reference to the vacuum level. The results showed a strong dependence of the band structure of eumelanin films on the processing protocols and the molecular structure of the monomers.

Second, we used atomic force microscopy (AFM) and conductive AFM to elucidate the nanoscale structure and electrical response of Sepia eumelanin. AFM images showed quasi-spherical granules featuring protrusions on their surfaces, with a width average of about 18.5 ± 6.4 nm and a height average of about 3.0 ± 1.6 nm. The protrusions are compatible with granule subunits considered in the hierarchical development of Sepia eumelanin, as proposed in the literature. C-AFM revealed for the first time a nanoscale electrical response of films formulated from Sepia eumelanin ink, indicating a charge carrier transport through intra- and inter-granular conduction paths. The results related to the band structure and nanostructures pave the way toward defining suitable eumelanin-metal electrode interfaces for efficient charge carrier injection and charge transport, owing to similarities between the supramolecular structure of DHI/DHICA synthetic films and that of Sepia at the protrusions length scale.

Finally, we proposed to explore by electron paramagnetic resonance spectroscopy and magnetometry techniques the humidity-dependence magnetization of *Sepia eumelanin* pellets to shed light on the origin of its electrical response from the molecular level. Preliminary results are presented in Appendix A of this thesis. *Sepia eumelanin* pellets exhibited the coexistence of ferromagnetic and paramagnetic behaviour at room temperature, with a magnetization that decreases at high humidity.

The findings of this PhD thesis provide insights into the structure-property relationship of bio-sourced materials, strategic for sustainable organic electronics.

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LIST OF ACRONYMS AND SYMBOLS

ACRONYMS

AFM: Atomic Force Microscopy.

AISSP: Ammonia-induced solid-state polymerization.

C-AFM: Conductive Atomic Force Microscopy.

CB: Conduction band.

DHI: 5,6-dihydroxyindole.

DHICA: 5,6-dihydroxyindole-2-carboxylic acid.

EIS: Electrochemical Impedance Spectroscopy

EPR: Electron Paramagnetic Spectroscopy.

HB-AFM: Hybrid-mode Atomic Force Microscopy.

HRFs: Halogenated Flame Retardants.

HQ: Hydroquinone

HOMO: Highest Occupied Molecular Orbital.

IPES: Inverse Photoemission Spectroscopy.

IQ: Indolequinone.

LUMO: Lowest Unoccupied Molecular Orbital.

M-SC: Metal-Semiconductor.

OECT: Organic electrochemical transistors.

OFETs: Organic Field Effect Transistors.

OLEDs: Organic Light Emitting Diodes.

OPV: Organic Photovoltaics.

OSs: Organic Semiconductors.

ppm: parts per million.

PVB: Polyvinyl Butyral.

QI: Quinone Imine

SC: Semiconductor.

SCLC: Space Charge Limited conduction.

SEM: Scanning Electron Microscopy.

SQ: Semiquinone.

TEM: Transmission Electron Microscopy.

UHV: Ultrahigh vacuum.

UPS: Ultraviolet Photoemission Spectroscopy

VB: Valance band.

VNA: Vector Network Analyzer.

VSM: Vibrating Sample Magnetometer.

WEEE: Waste Electrical and Electronic Equipment.

SYMBOLS

ϕ_B : Schottky barrier.

q: elementary charge (1.602×10^{-19} Coulomb).

χ_e : Electron affinity.

E_I : Ionization energy.

E_g : bandgap energy

E_F : Fermi level.

E_{vac} : Vacuum level.

ϕ_M : Metal work functi

ϕ_S : Semiconductor work function.

μ_B : Bohr magneton (9.274×10^{-24} J. T⁻¹)

χ : Magnetic susceptibility

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CHAPTER 1 INTRODUCTION

1.1 Research context

The development of organic semiconductors (OSs) has established the field of organic electronics with successful achievements in applications such as flexible sensors [1], organic light-emitting diodes (OLEDs) [2, 3] organic thin film transistors (OFETs) [4], organic photovoltaics (OPV) [5, 6], and organic photodetectors [6].

OSs are carbon-based molecular materials possibly including heteroatoms such as N, O, S, ... in their molecular structures. OSs can be polymers [7] or small molecules [8, 9]. Their optoelectronic properties (e.g. their optical band gap) can be tuned through chemical synthesis. [10] [11]

Green organic electronics is an emerging field where organic molecular materials extracted from natural sources (bio-sourced), obtained from organic waste valorization, or synthesized by green chemistry principles are explored for their charge carrier transport properties to design and develop environmentally benign, biodegradable technologies and devices [12]. Green organic electronics could help to alleviate the crisis of Waste Electrical and Electronic Equipment (WEEE, about 60M tons accumulated each year [13]). WEEE contains hazardous materials that still remain poorly managed [14].

This Ph.D. thesis is in the field of Green Organic Electronics. The object of the research is eumelanin, the black-brown member of the melanin family of pigments, ubiquitous in the biosphere [15]. Sepia eumelanin (from now on indicated as Sepia), a type of eumelanin extracted from the ink of the cuttlefish (i.e., *Sepia officinalis*), is a potential candidate for Green Organic Electronics. It features a hierarchical structure that includes nanometric granules. Sepia has been investigated for its biodegradability in industrial compost conditions [16].

Our motivation to study eumelanin is its electrical response [17, 18]. The material exhibits a hydration-dependent electrical conductivity. Its protonic conductivity increases with relative humidity [18-20] whereas the electronic one is predominant in anhydrous conditions [17]. However, our knowledge of the material needs further elucidation on structure-property relationships. In particular, the location of the transport energy levels, the origin of its charge carrier transport and magnetic properties must be well understood.

In general, bio-sourced materials are intrinsically hydrated and contain ionic species (e.g., Na^+ , Cl^- , K^+ , Ca^{2+} , and H^+) [21]. Several of them, including eumelanin, are studied for their mixed ionic-electronic conductivity [21-24]. The design and implementation of applications based on the use of mixed conductors require a fundamental understanding of their properties such as ionic transport, electronic transport, and ionic-electronic coupling which could go beyond the knowledge of conventional organic semiconductors or proton conductive polymers. The device performance and applications are a result of a complex interplay between the processing methods, the nano-microstructures, the nature of the metal electrodes and the environmental conditions [25].

Literature reports that eumelanin has binding sites for metal ions such as Ca^{2+} , Mg^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , etc [26]. The role that the presence of such ions might play in the electrical and magnetic properties of the biomacromolecule is undiscovered. In this context, our research addresses the eumelanin magnetic properties to provide insights into the correlation between the electron spins and the electrical response. Hence, this Ph.D. thesis also paves the way for the possibility of developing devices operating based on the magnetic behaviour of eumelanin.

As *Sepia* eumelanin is made of nanometric granules (100-200 nm), a nanoscale study is deemed necessary to shed light on the intra- and inter-granular charge carrier transport.

1.2 Band structure in organic semiconductors

In OSs, the bonding between carbon atoms creates molecular orbitals, associated with electronic states. Atomic orbitals with sp^2 character overlap to form strong bonds, called σ -bonds. The electrons participating in such bonding are highly localized between the two atoms and do not contribute to any electrical conductivity. Differently, π -orbitals resulting from the coupling of p_z orbitals are delocalized over several atoms and enable electrical conductivity (see Figure 1.1).

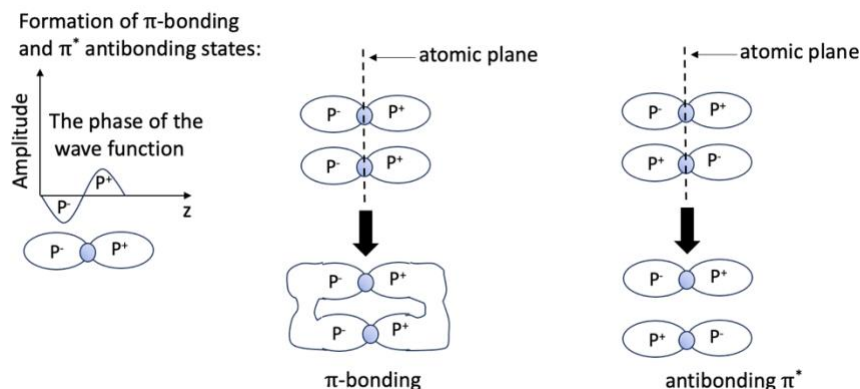


Figure 1.1 A schematic illustration of coupling between two p_z orbitals. Z is the direction associated with electronic wavefunctions perpendicular to the atomic plane; p^- and p^+ represent respectively the negative (-) and positive (+) parts of the wavefunctions that either interfere constructively or destructively, adapted from [27].

Two types of states are formed when p_z orbitals interfere, namely “ π –bonding” and “ π^* -antibonding” states. The orbitals (states) that enhance the overall bonding and stabilize it are the low energy states (bonding or “valence” states). States that destabilize the bonding when occupied are high energy states (anti-bonding or “conduction” states) (See Figure 1.2 (a)) [28]. Valence states are fully occupied and conduction states are unoccupied at a low level of doping or impurities and a low-temperature [29].

The band structure of OSs originates from the interaction of the π -orbitals of the repeating units (building blocks) throughout the polymer or small molecular chains in the solid state. A conjugate structure, which creates continuous electron transport, is formed by the overlapping of π -orbitals across σ -bonds. We thus obtain electronic delocalization when there are alternating single and double bonds in the molecular chains (see Figure 1.2 (b)). The addition of a molecule or polymer unit to the chain induces the hybridization of electronic states. Several additions of building blocks yield to more and more energy levels, thus forming energy bands rather than discrete energy levels as exemplified in Figure 1.2 (c) [30, 31].

The HOMO-LUMO gap (E_g) (analogous to band gap in inorganic semiconductors) is then defined as the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), typically ranging from 1.0-3.0 eV. The HOMO and LUMO (frontier) orbitals are respectively referred to as valence band (VB) and conduction band (CB)-edges associated with the gap energy. According to the scheme in Figure 1.2 (c), E_g decreases with

the extension of the length of π -stacked molecular units. This means, that for materials designed to explore properties related to energy levels at the molecular scale, E_g will be different from that of solid-state thin films at the micrometric scale.

The conjugation structure (i.e., the alternation of single and double C-bonds polymer backbone) is important for OSs because it determines the electronic properties of the material. OSs are made up of conjugated molecules with π -electron delocalization, which allows for charge transfer and electrical conductivity. The length and nature of the conjugated structure can affect the energy levels of the material, which in turn affects its electronic properties and potential applications in organic electronics, such as solar cells, light-emitting diodes or transistors. Additionally, the conjugation structure can also impact the material's optical and mechanical properties as well as its solubility and processability, which are important factors for practical applications. A more extended conjugation is suitable for charge transport properties [32]. Therefore, understanding and controlling the conjugation structure is crucial for developing efficient and reliable organic electronic devices. There are numerous factors affect the energy gap E_g such as conjugation length, aromaticity, planarity, substituent effects, and intermolecular interactions related to the conjugated polymer backbone [33, 34].

The width of both valence and conduction states (i.e., the spectra of energy levels of occupied and unoccupied orbitals) in OSs is generally about two orders of magnitude lower (< 100 meV, typically a few $k_B T$ at room temperature) than that of their inorganic counterparts. This is because conjugated polymers are weakly bonded macromolecules with several degrees of conformation freedom. As a result, one has microstructures with different degrees of molecular order varying from completely amorphous to crystalline depending on molecular nature, the processing and/or post-treatment [35-37]. Mostly, OSs feature structural disorder that induces localized states and thus small widths of valence and conduction bands.

The π -electron delocalization can also occur through π - π stacking between adjacent planes of covalently bonded molecular ring compounds (as shown in Figure 1.3). This is especially desirable in the processing of small molecules into solid-state crystals [38]. It has been shown that the charge carrier transport by charge-hopping through overlapping wavefunctions of the neighbouring planes is predominant in oligomeric systems while the intrachain transport is likely observed in conjugated polymers [38]. Such an extent of overlap also increases the charge carrier mobility. To improve

mobilities, organic crystals engineering has so far focused on the control of intermolecular interactions to assemble molecules into a specific solid-state arrangement with efficient π - π overlap leading to desired physicochemical properties of semiconductor molecules [38].

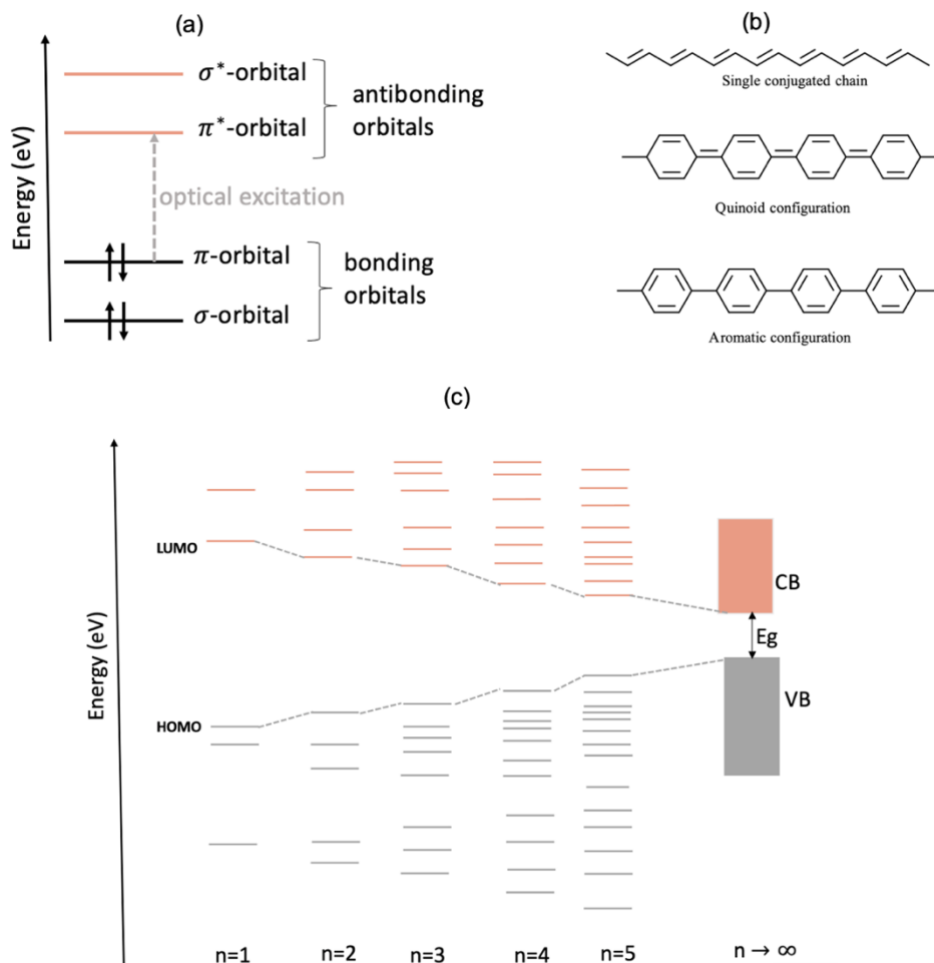


Figure 1.2 (a) The energy levels of a π -conjugated molecule. The lowest electronic excitation is between the bonding π -orbital and the antibonding π^* -orbital [37]. (b) Different configurations of the conjugated molecule chains give rise to electronic delocalization along the segment chain. In the aromatic form, electrons mainly localize in the aromatic ring. In the quinoid form, electrons can transfer across the bridging covalence bond, leading to lower energy than that of the aromatic form. (c) Formation of band structure as a combination of several molecular energy levels through conjugation in organic semiconductors, with n the of repeating molecular units [30].

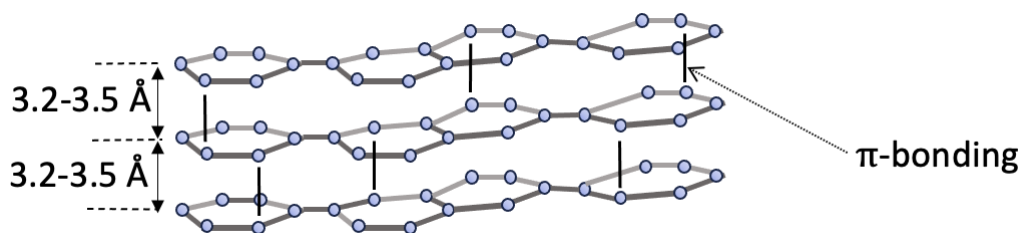


Figure 1.3 Interplanar pi-pi stacking between planar oligomer structures, establishing the conduction electrons (adapted from [38]).

1.3 Charge carrier injection

Metal-Semiconductor (M-SC) contacts are present in modern electronic and optoelectronic devices. The charge carrier transfer process from one material to another at the metal electrode-semiconductor interface depends on their energy band structures. These contacts are then critical for device reliability and performance. In organic semiconductors (OSs), where the intrinsic carrier density is very low ($n_i \ll 10^{10} \text{ cm}^{-3}$) [37], charge carrier injection from contacts is one of the means to increase the carrier concentration and achieve electrical conductivity high enough for the device application [39, 40].

To understand charge carrier injection, one must consider the parameters associated with the energy levels, namely the work function (ϕ_M), the Fermi level (E_F) and vacuum level (E_{vac}) positions, energy gap (E_g), ionization energy (E_I), and electron affinity (χ_e), which are important for any electronic material. In solid-state physics, the Fermi level is the energy state for which the occupation probability by an electron is 50% at any temperature. It represents the energy required to add one fermion to the system at 0 K. The work function (ϕ_M) is the energy required to bring an electron from the Fermi level to the vacuum level (see Figure 1.4 (a) and (d)). E_{vac} is the energy level of an electron positioned at rest with respect to the sample within a few nanometers outside the solid (i.e., a sufficient distance for the electron to experience the full impact of the surface dipole).

In a metal, E_F marks the highest occupied energy level with a continuum of states, formally making ϕ_M equal to both E_I and χ_e at very low T near 0 K. On the other hand, the semiconductor (SC) has generally no electrons at the Fermi level, which typically lies between the bandgap edges and its position depends on the temperature, the carrier density, and the doping concentration [40].

The work functions of the metal and semiconductor are usually different. While making the M-SC electrical contacts, there is a flow of electrons from the lower work function material to the higher work function one to reach equilibrium. The Fermi levels will align in thermal equilibrium. Such charge carrier transfer will create a built-in potential V_{bi} associated with the resulting space charge region, which leads to the energy band bending structure in the same manner as the p-n junction.

During the device processing, it is desired to establish the so-called “ohmic contact” that, in the presence of an applied electric field, provides a very low electrical contact resistance, allowing conduction in two senses (M->SC, SC->M). One method to make ohmic contact is to use the materials with $\phi_M < \phi_S$ for electron-type majority carriers and $\phi_M > \phi_S$ for hole-type majority carriers (see Figure 1.4 (c) and (f), ϕ_S : the workfunction the SC). Another strategy consists of heavily doping the surface of the semiconductor to create a tunnelling barrier when the space charge region becomes very small (≤ 5 nm) [41].

However, ohmic contacts are not always easy to obtain. In addition to the work function, other properties such as high electrical conductivity and chemical reactivity should be also considered when selecting a metal as an electrode for solid-state devices. Therefore, we often deal with contacts where $\phi_M > \phi_S$ for an n-type semiconductor and $\phi_M < \phi_S$ for a p-type semiconductor. In both cases, there is an energy barrier ϕ_B between the two materials in contact as predicted by the Schottky-Mott model. It requires enough energy for charge carriers to overcome the barrier and pass from the Fermi level of the metal to the minimum of the CB (E_C) or maximum of the VB (E_V). The model implies a linear dependence between the barrier height and metal work function (ϕ_M) defined as the energy difference given by equations (1.1) and (1.2), respectively for electrons and holes [42, 43].

$$\phi_{B,e} = \phi_M - \chi \quad (1.1)$$

$$\phi_{B,h} = \phi_M - \phi_S \quad (1.2)$$

It has been reported that a barrier $\phi_B > 0.2$ eV will form a high contact resistance that significantly limits the device's electrical response [44].

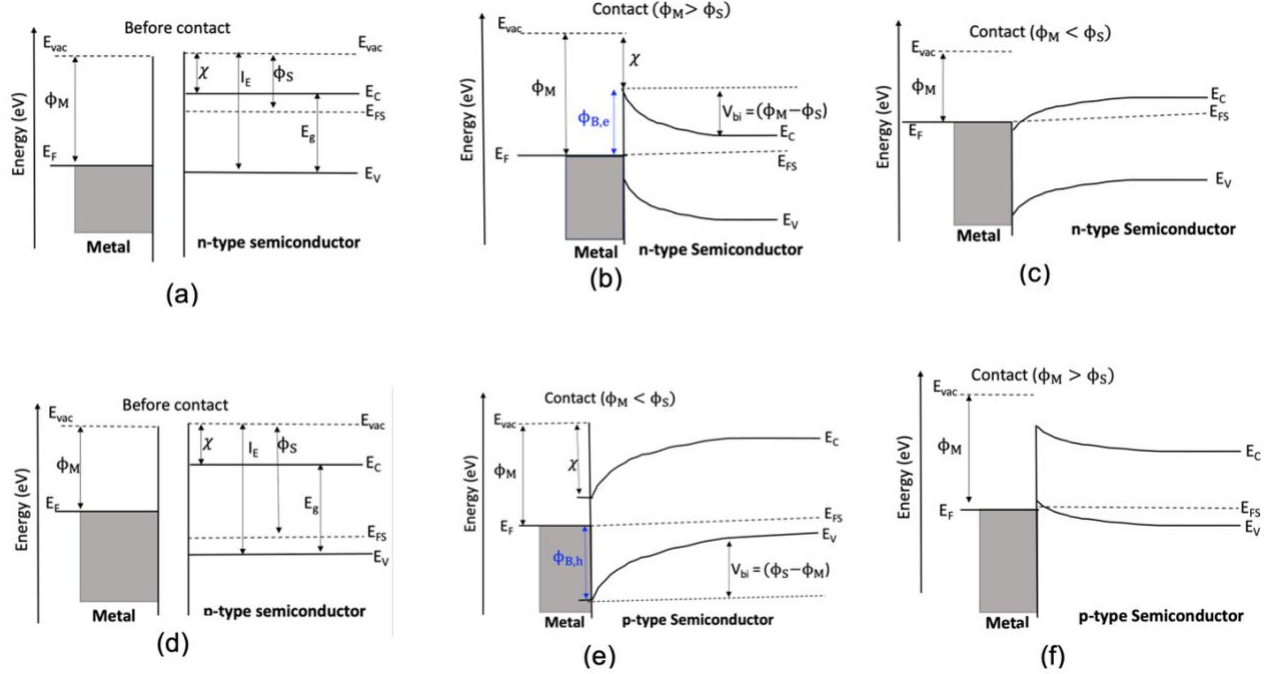


Figure 1.4 Energy band structure of (a) metal-n-type SC and (d) metal-p-type SC, before contact. Formation of the Schottky barrier and the built-in-potential barrier at the M-SC junction for (b) electron and (e) hole charge carriers. Formation of M-SC ohmic contacts with a (c) n-type SC and (f) p-type SC. In organic semiconductors $E_C \equiv \text{LUMO}$ and $E_V \equiv \text{HOMO}$.

Figures 1.4 (b) and (e) indicate $\phi_{B,e}$ ($\phi_{B,h}$) as being a barrier seen by the majority charge carriers moving from metal-to-semiconductor and V_{bi} the barrier seen by the majority charge carriers from the semiconductor-to-metal. The former cannot be influenced by the external electric field while the latter can be. Under the forward bias¹ condition, V_{bi} will be reduced by the applied voltage (i.e., $V_{bi} - qV$) while the reverse bias² will increase it (i.e., $V_{bi} + qV_R$, $q = 1.602 \times 10^{-19} \text{ C}$). On the other hand, in Figures 1.4 (c) and (f), showing the ohmic contacts, the effective barrier is quite small and there is conduction in both directions whatever the bias conditions. The Schottky barrier as described thus causes problems in the development of electronic devices.

In research on establishing the transport physics to overcome the barrier ϕ_B , one should be aware that the Schottky-Mott model could incorrectly predict the experimental results since it neglects

¹ Forward bias condition in M-SC junctions refers to as the applied positive voltage to the metal with respect to n-type semiconductor or a positive bias to the p-type semiconductor with respect to the metal.

² The reverse bias is opposite to the forward one.

different types of physical and chemical interactions that are practically hard to avoid at the interfaces of two dissimilar materials. There might be surface states or gap states within the semiconductor bandgap induced by surface dangling bonds, defects, or chemical disorder at the interface, which pin the Fermi level at a fixed position. As a result, the energy barrier height ϕ_B becomes independent of the work function for various metal electrodes [43, 45].

Overall, the goal is always to avoid or reduce as much as possible the work function differences which are also the origin of band bending, to achieve the ohmic behavior which gives a higher electrical response for a conductive material. This can be done by choosing suitable electrodes according to the conditions regarding the metal work function. It means, for organic electronic devices (also valid for any semiconductor), it is wise to measure both the electron affinity and the ionization energy which, respectively give the location of the LUMO and HOMO levels of the semiconductor thin film. It is mainly the first step to improve the injection of charge carriers into the semiconductor active layer to study electronic transport not limited by electrical contacts. The phenomena leading to the pinning of the Fermi level can then be explored by both microscopic and spectroscopic studies to find out if optimization of the interface structure is required. In other words, it would be important to study the possible formation of surface states which could limit the applicability of the Schottky model.

Several techniques can be used to characterize the formation of surface states that lead to Fermi-level pinning in a semiconductor material such as Kelvin Probe Force Microscopy (KPFM), X-ray photoelectron spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Overall, a combination of these techniques can provide a comprehensive understanding of the formation of surface states and Fermi-level pinning in semiconductor materials.

For eumelanin, the subject of this thesis, the electrical properties are not well known nor are the type of majority carriers (i.e., holes or electrons?). The starting approach is to explore where HOMO and LUMO are located. Afterwards, it could be possible to consider two metals, one of which is expected to enhance the injection of holes and the other that of electrons.

1.4 Charge carrier transport

Once injected from the M-S contact, charge carriers must move within the semiconductor to reach the collecting electrode and thereby give an electrical response from the device. It is then fundamental to understand the transport physics to optimize the charge carrier mobility.

In OSs, the charge carrier transport mechanism is determined by intermolecular electronic coupling resulting from the spatial overlap of molecular orbitals of adjacent molecules [46]. In crystalline OSs, there is delocalization of charge carriers which is limited to a few molecules. The band-like transport is then used where the charge carriers are only occasionally scattered by lattice vibrations or impurities [47]. In the band-like transport, the free electrons are mainly moving at the bottom of the conduction band, i.e., at the LUMO level, (see Figure 1.5 (a)) while the free holes are at the top of the valence band near the HOMO level. The mobility in organic crystals is typically measured in the range of $10^{-1} - 10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [48, 49].

However, the manufacturing of pure organic crystal samples is difficult to achieve as the inherent weak intermolecular interactions in OSs easily induce defects during processing [50]. Therefore, most developed organic semiconductors, which are preferably solution-processed, exhibit a more amorphous than crystalline structure. This leads to localized states in the band gap that can trap charge carriers. In general, it is understood that charge carrier transport takes place between localized states in OSs [51, 52].

The transport model which is commonly proposed in the literature is the phonon-assisted hopping [51, 53-55]. Charge transport occurs through successive hops between molecules from a localized state i to a localized state j with the aid of phonon absorption. The hopping rate W_{ij} is given by the Miller-Abrahams relation a

$$W_{ij} = \nu_0 \exp(-2\gamma|R_{ij}|) \begin{cases} \exp\left(-\frac{\varepsilon_j - \varepsilon_i}{k_B T}\right), & \varepsilon_j > \varepsilon_i \\ 1, & \varepsilon_j < \varepsilon_i \end{cases} \quad (1.3)$$

in which ν_0 is the attempt hopping frequency, γ is the inverse radius of localization which represents the overlapping of the electronic wavefunctions of the two molecules; R_{ij} is the distance between sites i and j ; ε_i and ε_j are the energies of initial and final states, respectively. Nevertheless, using M-A rates is only valid for weak electron-phonon coupling and low temperatures [56, 57]. This corresponds to hopping activation energy comparable to the thermal excitation energies of single phonons (typically less than 0.07 eV) and single molecular vibrations is ($< 0.15 \text{ eV}$) [53, 58].

The factor that is not accounted for in equation (1.3) is the polaronic nature of charge carriers. By definition, a polaron is a quasiparticle consisting of an electron or hole that couples to phonons

associated with ionic vibrations [59, 60]: “An excess charge injected into a polarizable solid displaces the ions in its neighbourhood and creates a polarization cloud that follows the charge carrier as it propagates through the crystal” [59].

The transition from site i to site j is described as the motion across the spatial configuration coordinates. This is enhanced by the molecular motions that will bring the states ε_j (unoccupied) and ε_i (occupied by a polaron) to a similar configuration [61]. It is important to note that this leads to a significant decrease in the hopping activation energy barrier E_a (i.e., the minimum energy required for an electric charge to hop between two localized states in the material) as shown in Figure 1.5 (b). Charge transport then happens by hopping between neighbouring sites where an adjusted neutral molecule adopts the configuration of a charged molecule under an applied electric field [62]. Figure 1.5 (c) shows an example of a hole-like polaron moving along the conjugation-broken polymer backbone [63].

There are two kinds of polarons (small and large), classified based on the spatial extent of the polarization cloud, i.e., the range action of the electron-phonon interaction. Large polarons are attributed to long-range electron-phonon interaction (i.e., polaron radius $\gg$ lattice parameter) with carrier mobility decreasing with temperature, quite similar to that of free electrons or holes [59].

On the other hand, small polarons correspond to short-range electron-phonon coupling (i.e., polaron radius comparable to the lattice spacing) with a thermally activated mobility ($\ll 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) [59]. The polaron transport, which is dependent on the binding energy, is a phonon-assisted hopping, characterized by an exponential increase of the conductivity σ with temperature T , following the Arrhenius behaviour [64] given by equation (1.4). The binding is large for small polarons which are highly localized and interact strongly with the crystal lattice, while large polarons are more delocalized and interact weakly with the polarizable environment in the material.

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (1.4)$$

In conclusion, the range of order disorder seems to determine the transport mechanism in OSs. The polaronic transport is dominant in their film forms due to their likely inevitable structural disorder. There are several experimental results that evidence the presence of polarons in a wide range of materials such as transition metal oxides [65], organic semiconductors [56, 66, 67], conducting

polymers [68], amorphous compounds [69], perovskites [60, 70], etc. However, current observations in different phenomena are not enough to confirm the ubiquity of polarons.

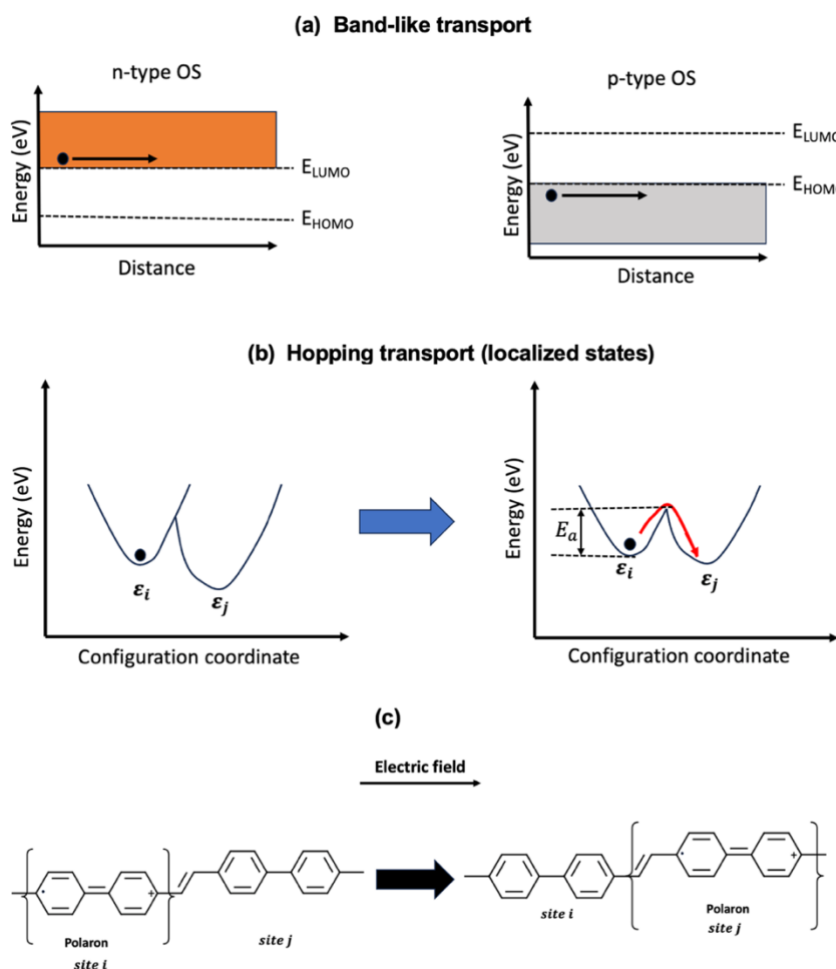


Figure 1.5 Schematic representation of (a) band-like transport model in n-type semiconductor [47] and (b) hopping transport model in OSs. (b) indicates potential energies corresponding to initial (ϵ_i) and final (ϵ_j) polaronic states involved in the charge carrier transfer process under an applied bias. The left shows the two states separated and, on the right, the combined potential lowering the hopping activation energy E_a . The charge carrier and hopping direction are represented by the black sphere and the solid red arrow, respectively. (c) A simplified scheme of hole-like polaron transport in a conjugated backbone, adapted from [63].

Nowadays, establishing the transport physics in films of conductive organic solids remains an open question and several materials have been studied. A transport model that considers the temperature, electric field, and carrier concentration as parameters of mobility ($\mu(T, E, n)$) is still needed. The mechanism is more poorly understood for bio-sourced materials which lack chemical control of

the molecular structure, leading to unknown supramolecular structure. They can sometimes be electronic-ionic mixed conductors (e.g., eumelanin) where the generation of carriers, as well as the transport mechanisms, are not yet revealed. Eumelanin is an interesting biomaterial whose study of the transport of charge carriers will be essential to understand the behaviour of its electrical conductivity.

1.5 Research objectives

Despite its interest in sustainable electronics, the origin of the electrical response of the bio pigment eumelanin is still largely unknown. The main objective of this Ph.D. thesis is to study the band structure, nanoscale structure, and magnetic properties of eumelanin to shed light on the origin of its electrical response and possible semi-conductivity. The specific objectives of the thesis were defined as follows:

- Study the band structure of eumelanin for locating the HOMO and LUMO energy levels of chemically controlled eumelanin building blocks. Samples were prepared by spin-coating solutions/suspensions of eumelanin building blocks on SiO₂ substrates. The work was done in collaboration with the research group of Professor Ian Hill at Dalhousie University (Halifax, Canada), who contributed with equipment and expertise in ultraviolet photoemission and inverse photoemission spectroscopy.
- Elucidate the relationship between the nanoscale structure of Sepia eumelanin and its electrical response using high-resolution atomic force microscopy (AFM) and conductive AFM. The measurements were carried out at NT-MDT Spectrum Instruments by their scanning probe microscopy scientists (Tempe, Arizona, USA).

1.6 Thesis structure

This thesis is divided into three parts:

The first part, which includes chapters 1, 2 and 3, consists of providing the reader with the knowledge allowing him/her to understand our approach in methodology and interpretation of the results in the second part.

The first chapter, which is the general introduction, underlines the importance of organic semiconductors, their energy band structure, factors involved in carrier injection such as the Schottky barrier and physical models for charge carrier transport in organic electronic devices. At the end of the chapter, we define our research objectives. The second chapter gives a literature review on eumelanin, the subject of this thesis, particularly its consideration in the field of green organic electronics, its supramolecular structure, and the state of the art on its electrical properties.

In the third chapter, we explain the working principles of the experimental setups, starting with the UPS and IPES spectroscopic methods which allowed us to study the electronic structure of the eumelanin layers. Then, we give a detailed description of the AFM techniques which allowed us to study the nanostructures of Sepia eumelanin as well as their electrical properties revealed by conductive AFM.

The second part of the thesis is composed of chapters 4, 5, 6, and 7 which present the experimental results as well as the analysis and interpretation. Chapter 4 discusses the structure of the energy bands, i.e., the HOMO and LUMO levels of the eumelanin films and their dependence on the atmosphere to which samples are exposed under ammonia-enriched atmosphere, oxygen- and humidity-controlled atmosphere, and vacuum after deposition. Chapter 5 covers a systematic study on the size distribution of sepia eumelanin nanoaggregates while giving a discussion of their electrical response. Chapter 6 provides a general discussion of the results presented in chapters 4 and 5 and chapter 7 summarizes the main findings, contributions, and perspectives for future studies.

The third part of this thesis (in Appendix A) focuses on the study of the magnetic properties of eumelanin by electron paramagnetic resonance spectroscopy (EPR) and magnetometry while we consider the effect of the humidity.

1.7 Published articles and conference abstracts during the PhD.

1.7.1 Articles

- 1) **Niyonkuru D.**, Carrière A., Ambrose R., Gouda A., Reali M., Camus A., Pezzella A., Hill I., Santato C. Locating the bandgap edges of eumelanin thin films for applications in organic electronics. *Journal of Chemical Technology & Biotechnology*. 2022 Apr;97(4):837-43. (Results are included in Chapter 04).

- 2) **Niyonkuru D.**, Camus A., Reali M., Gao Z., Shadrack D. M., Butyaev O., Surtchev M., Santato C. A nanoscale study of the structure and electrical response of Sepia eumelanin. *Nanoscale Advances*. 2023. (Results are included in Chapter 05)
- 3) Gao Z., **Niyonkuru D.**, Yelon A., Santato C. Effect of structure on semiconducting properties of a small molecule n-type organic semiconductor: Phenyl-C61-butyric acid methyl ester. *Journal of Vacuum Science & Technology A*. 2023 Jul 1;41(4).
- 4) Matos-Peralta Y., Reali M., Camus A., **Niyonkuru D.**, Molood H., Gao Z., Santato C. Nature as the Source of Materials for More Sustainable Organic Electronics, *Material Matters™* 2023, 18.1.

Chapters 4 and 5 present and discuss the results, namely figures and tables, published in articles 1) and 2), respectively. Figures and tables were included with the permission of the publishers.

1.7.2 Conference and seminar abstracts

- Oral presenter at the 31st International Materials Research Congress (IMRC, Fall 2023), Cancun, Mexico. "Insights into the nanostructure and electrical response of sepia eumelanin" by D. Niyonkuru, A. Camus, M. Reali, Z. Gao, D. Shadrack-Madulu, C. Santato. Symposium: "Sustainable Electronics: Eco-Design, Toxicology, Green Chemistry, Biosourced Materials, And E-Waste Management".
- Oral presenter at the 11th International Conference of the African Materials Research Society (AMRS, Fall 2022), Dakar, Senegal. "Nanoscale Insights on Sepia Melanin structure for sustainable organic electronics; D. Niyonkuru, A Camus, Manuel Reali, D. S. Madulu, O. Butyaev, M. Surtchev, C. Santato. Symposium: Nanomaterials, Quantum Materials, Photonics Materials & Nanotechnologies.
- Oral presenter at the International Conference of the American Chemical Society (ACS) Fall 2022, Chicago USA. Eumelanin biopigment: thin-film fabrication and location of the HOMO and LUMO levels by UPS and IPES; D. Niyonkuru, A. Carrière, R. Ambrose, A. Camus, M. Reali, A. Gouda, A. Pezzella, I. Hill, and C. Santato.

- Speaker to the Discovery Seminar of Chemical Engineering, Polytechnique Montreal, May 2022, Eumelanin pigments towards environmentally benign electronics, D. Niyonkuru, M. Reali, A. Camus, C. Santato.
- Oral presenter at Annual Fall Meeting of the NSERC- Green Electronics Network (GreenEN) probing the valence and conduction band edges in eumelanin thin films using UPS-IPES; D. Niyonkuru, R. Ambrose, I. Hill, C. Santato.

CHAPTER 2 LITERATURE REVIEW

2.1 Green organic electronics

The continuously increasing market demand for electric and electronic equipment (EEE) compels the electronics industry to constantly offer new products with improved service without enhanced lifespans. Such rapid technological evolution leads to the eventual disposal of old electronic products which are of no use, commonly referred to as waste electric and electronic equipment (WEEE) or e-waste. These include computers, televisions, laptops, refrigerators, headphones, cellphones, batteries, etc. Considering the worldwide scenario, approximately 44.7 million tonnes of e-waste were produced globally according to the United Nations report in 2016, and this amount has since reached 53.6 Mt (million tonnes) [71, 72]. This category of solid waste comprises valuable materials (gold (Au), iron (Fe), copper (Cu), silver (Ag), etc.) and also a range of hazardous elements such as lead (Pb), mercury (Hg), and halogenated flame retardants (HRFs), and so on [73, 74]. The presence of such toxic constituents in WEEE has raised significant concerns regarding their improper disposal on a global scale. On the other hand, recovering valuable metals from this economic waste typically involves hazardous and undocumented methods through incineration, acid leaching, and roasting, which is a threat to human health and contributes to environmental pollution as well as carbon footprint [75].

Green organic electronics is a multidisciplinary emerging research area aimed at alleviating the global e-waste problem by identifying compounds of natural origin and establishing cost-effective processing routes for developing bio-sourced or synthetic organic materials applicable in human- and environmentally-friendly electronics [76]. Organic electronic devices are considered to fall under the green organic electronics umbrella if they are associated with activities such as (i) using carbon-based materials with a low environmental footprint, (ii) using bio-derived or recycled materials, (iii) using biodegradable or recyclable materials, (iv) minimizing energy consumption, and (v) shifting from subtractive to additive manufacturing techniques [77]. Additive techniques involve the deposition of material on a substrate to build up a desired the film/pattern by adding material onto the surface. Subtractive techniques involve the removal of material from a substrate to create a desired pattern or film on the surface. Removing a material increase the waste and loss of materials, which is not sustainable.

As green electronics tackle the problem at different levels of the device's lifecycle, from raw materials to end-of-life scenarios, different approaches are currently adopted with successful results towards sustainable organic electronic devices. These include the printability of electroactive bio-sourced materials, which is an additive process allowing reduction of both the waste of material and manufacturing embodied energy [78], OFETs based on natural pigments or biodegradable molecules obtainable from biomass feedstock [79, 80], biopolymer dielectrics for OFETs [81, 82], eco-friendly substrates [83-85] that can be transparent for OLEDs [84, 85], and also recycling gold from e-waste using environmentally benign solutions for reuse in electronic devices [86].

This PhD thesis is indeed part of the field of green organic electronics. Eumelanin is among the environmentally benign materials for sustainable (green) organic electronics owing to its multifunctionality such as electrical conduction, its potential for biodegradability and its abundance in nature. Research has already explored the potential applicability of eumelanin in various types of electronic devices. These include batteries and supercapacitors [87, 88], photovoltaic cells [89], organic electrochemical transistors exploiting protonic transport (OECTs) [90], and implantable medical devices exploiting the biocompatibility [91, 92].

However, one of the factors that greatly hinders the development of organic green electronics is the low electrical conductivity of biobased materials (e.g., eumelanin,) that requires a fundamental understanding of their properties to design alternative green materials featuring electronic conductivities comparable to that of high-performance organic semiconductors.

2.2 Eumelanin

2.2.1 Molecular structure and hierarchical build-up

Eumelanin is the black-brown pigment belonging to the melanin group, ubiquitous in the biosphere and can be found in a wide range of biological systems such as the human body and other mammals, cephalopods, insects, bacteria, and plants [93-95]. Its structure derives from dopaquinone which is a precursor directly formed by oxidation of the amino acid L-tyrosine by tyrosinase as illustrated by the scheme in Figure 2.1 [96]. In the absence of sulfhydryl compounds, dopaquinone is very reactive which gives rise to the addition of intramolecular amino groups to produce cyclodopa. During melanogenesis, cyclodopa undergoes a redox exchange with dopaquinone leading to the formation of dopachrome, which in turn rearranges to form mostly 5,6-dihydroxy indole (DHI) and

5,6-dihydroxy indole-2-carboxylic acid (DHICA). These dihydroxyindoles are then oxidized and polymerized to produce eumelanin [97-99]. The formation of dopa during this process is attributed to the reaction that produces dopachrome [99].

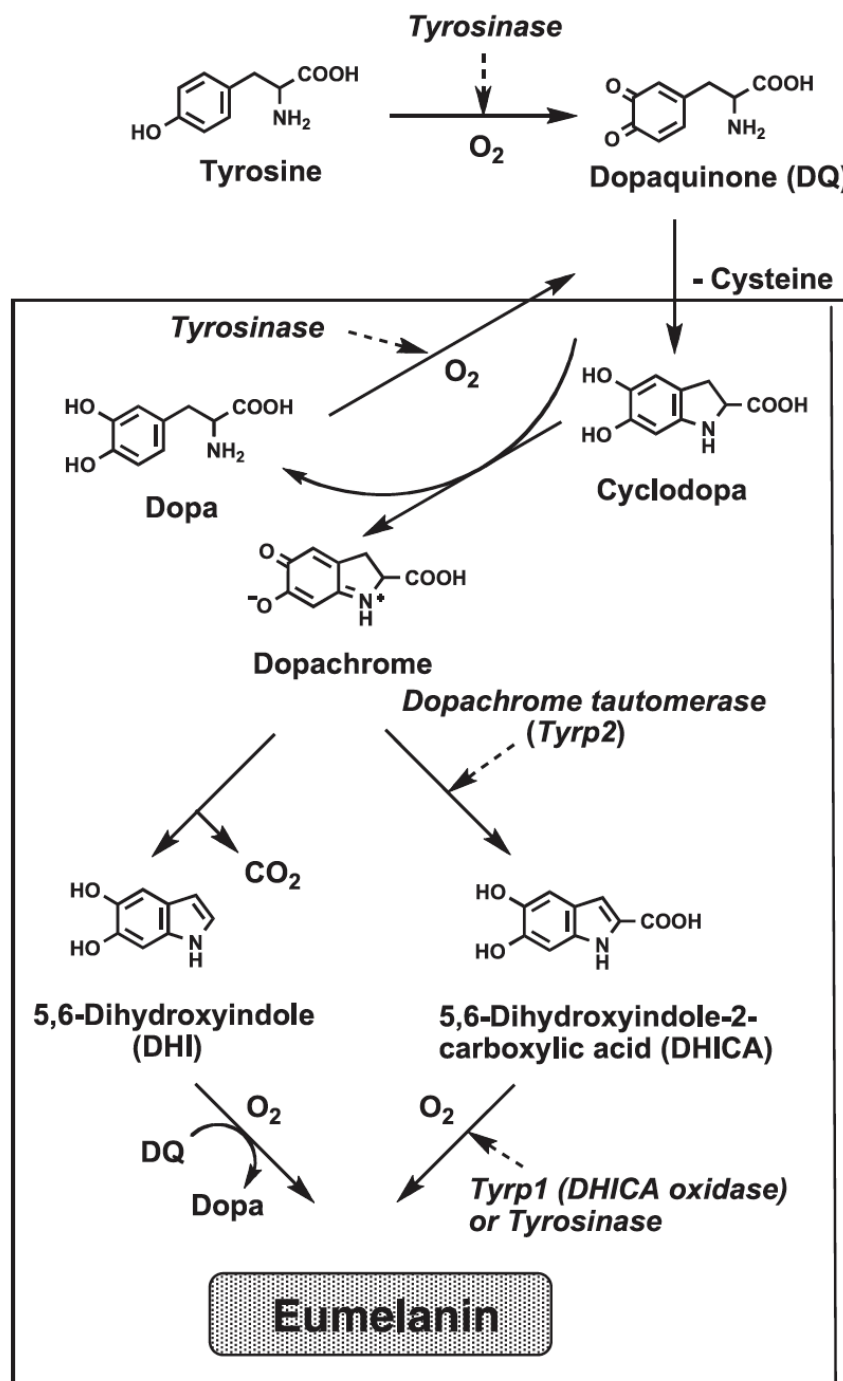


Figure 2.1 Biosynthetic pathways leading to eumelanin production. Reproduced from [99] with permission of John Wiley and Sons.

The DHI and DHICA monomers and their redox forms, namely indolequinone (IQ), semiquinone (SQ), hydroquinone (HQ) and quinone imine (QI) coexist in eumelanin macromolecules. Covalent bonding between these monomers (building blocks) forms oligomers. As the monomers have several polymerization sites (C2, C3, C4, C7, see Figure 2.2 (a)), different degrees of oligomerization are possible.

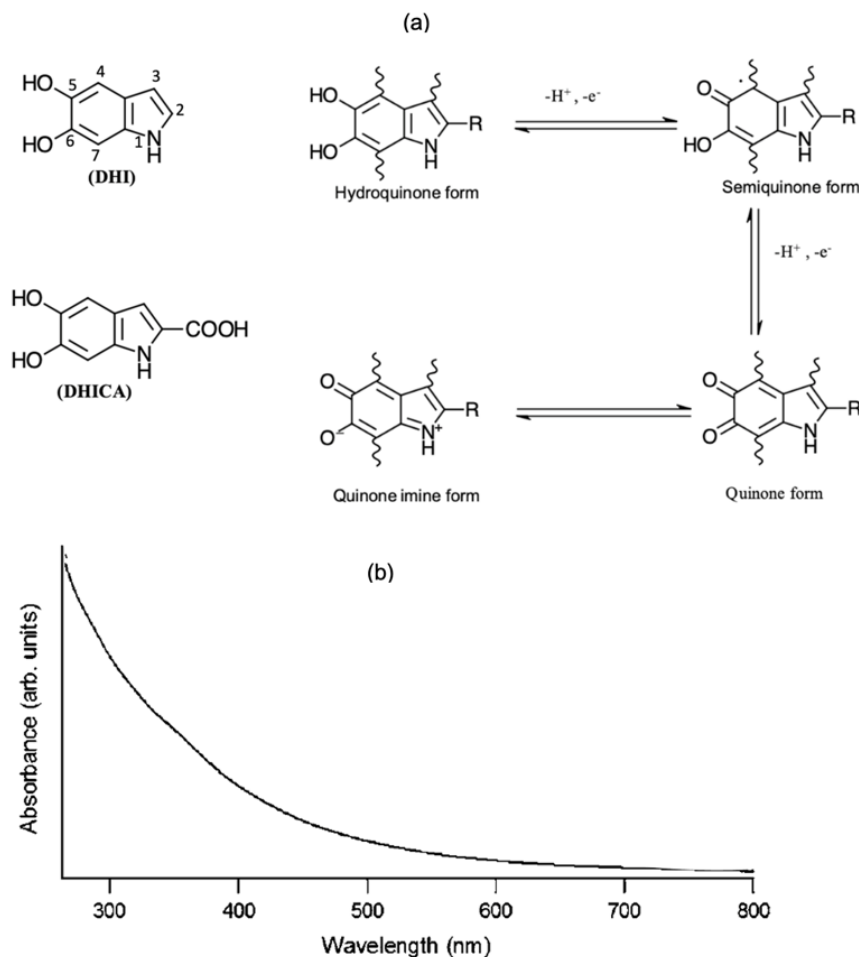


Figure 2.2 (a) Building blocks (monomers) of eumelanin and their redox forms. 5,6-dihydroxyindolequinone (DHI) or hydroquinone, 5,6-dihydroxyindole 2-carboxylic acid (DHICA), indole-quinone (IQ), and quinone-imine (QI) and semiquinone (SQ), -R is -H for 5,6-dihydroxy indole (DHI) and -COOH for 5,6-dihydroxy indole-2-carboxylic acid (DHICA) [100]; (b) characteristic broadband absorption of eumelanin which is more attributed to amorphous semiconductors than organic pigments [101].

Theoretical studies propose structural models to describe the functional properties of eumelanin, such as the broadband optical absorption extending from the UV to the near IR regions of the electromagnetic spectrum. The stacked oligomeric model [102-105] proposes that DHI-based tetramers form stable planar structures which further interact mainly by $\pi - \pi$ stacking, to generate eumelanin constituent units or protomolecules with a finite size of about 4-5 planes, (with an interplane distance of about 3.4 Å) and lateral extension of about 20 Å. This model is supported by experimental observations [106-108]. The absorption spectrum would be the result of electron delocalization during the in-plane polymerization, and electronic band extension resulting from stacked layers [109].

The absorption optical properties of eumelanin are explained by the geometric order and disorder model proposed by Chen et al. [110]. The term “order” corresponds to stacked planar layers while “disorder” is associated with random orientations of protomolecules and rotational disorder of molecular segments within the supramolecular structures. This model includes the excitonic interactions among eumelanin protomolecules arising from the interplay of geometric order and disorder characteristics of eumelanin aggregate structures. An exciton is defined as a quasiparticle formed by an electron-hole pair where the two particles remain bound together by coulombic interactions. Exciton-exciton interactions, which can be coulombic hole-electron exchanges between stacked eumelanin oligomers, become significant due to the short interlayer distance ($\sim 3-4$ Å), allowing the exciton radii to extend over several neighbouring molecules. Strong excitonic couplings broaden the absorption spectrum, giving rise to a monotonic increase of absorption towards shorter wavelengths as indicated in Figure 2.2 (b) [110]. Such a model is also in good agreement with the aggregated structures observed using the X-ray diffraction method, which revealed fundamental "particle" domains with a dimension of approximately 15 Å, consisting of a semi-crystalline arrangement of disordered planar structures formed by 4-8 DHI monomers, featuring a stacking spacing similar to graphite, around 3.45 Å [111, 112].

The ultrafast hole burning spectroscopic study recently conducted by B. Köhler et al. showed that the absorption spectrum of eumelanin is broadened because of chemical heterogeneity attributed

to chromophores³ that vary in the size of their sp^2 –hybridized domains [113]. The diverse set of chromophores exhibited a common photoinduced absorption spectrum and follow similar kinetics due to the rapid formation of immobile charge transfer excitons among the graphene-like chromophores, which decay locally in under 200 femtoseconds [113]. Their observations are consistent with geometric order and disorder model proposed by Chen *et al.* [110] and there may be other factors such as redox states or packing disorder that could also contribute to eumelanin absorption behavior. It is still unclear whether these chromophores are discrete molecular units or domains within large structures such as oligomers or polymer chains.

Experimental studies using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) revealed different structures of synthetic DHI-eumelanin and DHICA-eumelanin produced by oxidative polymerization of DHI and DHICA units, respectively. DHI-eumelanin is amenable to forming particle-like aggregates with a diameter of 10-50 nm via physical interactions between protomolecules [114, 115] and this is consistent with the above-mentioned theoretical studies. On the other hand, the distinct characteristics of DHICA-eumelanin arise from its carboxylic functional group that causes a twisting of inter-ring dihedral angles thereby reducing electrostatic interactions. Hence, the resulting oligoindole chains bundle together through hindered and interrupted π -conjugation. This leads to the formation of rod-shaped structures, exceeding 100 nanometers in length [94, 116]. It can be understood that the presence of the two monomers (i.e., DHI and DHICA) in bio-sourced eumelanin leads to a more complex structure difficult to elucidate.

Presently, eumelanin is assumed to be a chemically disordered (heterogeneous) macromolecule, characterized by polymorphic π - π stacked regions in the supramolecular structure, such that eumelanin exhibits structural disorder. A recent structural evaluation of natural eumelanin reported by Xiao *et al.* showed that the development of the macromolecules and thus, the morphological structure depends on the environment (i.e., organism) hosting the pigment [117].

Sepia eumelanin exhibits a hierarchical structure through different levels starting from its DHI and DHICA building blocks, followed by planar oligomers, protomolecules, supramolecular aggregate subunits, and granules [102]. Further experimental studies are needed to complement theoretical

³ A chromophore is part of a molecule or a chemical compound that is responsible for its color and can absorb and reflect specific wavelengths of light.

studies which are mostly limited to small oligomeric systems ($< 100 \text{ \AA}$) and have been often adapted to simplified systems with one type of building block, typically DHI. This does not give direct predictions for intermediate and large-scale structures ($> 10 \text{ nm}$) as we would like in sepia eumelanin. A complete structural model for natural eumelanin should include DHI-, DHICA-, and mixed DHI/DHICA-based oligomers.

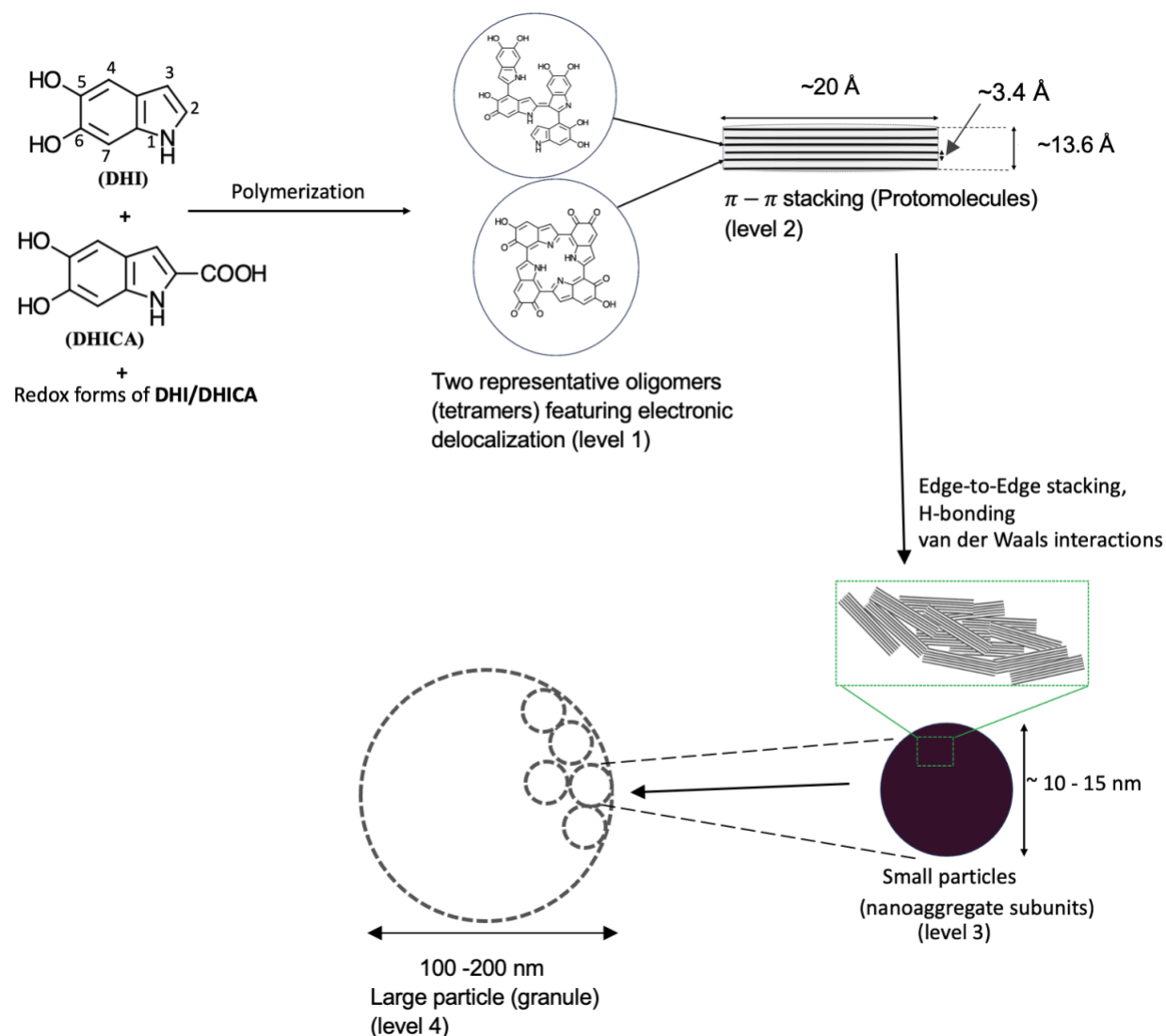


Figure 2.3 A simplified scheme illustrating the hierarchical structure of sepia eumelanin.

From *Sepia* eumelanin, structural units (small particles) of 10 -15 nm were observed by Scanning Electron Microscopy (SEM) and AFM [118-121]. They can be tentatively ascribed to self-assembled protomolecules through edge-to-edge π - π stacking and H-bonding interactions. Further aggregations from these units form large particles of 100-200 nm that can be associated with granules observed by Transmission Electron Microscopy (TEM), SEM or AFM images [118-123]. Figure 2.3 represents a simplified diagram depicting the supramolecular arrangement of *Sepia* eumelanin, leading to a hierarchical structure.

Despite considerable efforts in experimental and theoretical studies on elucidating eumelanin structures, understanding the structure-property relationship, such as the mechanisms of charge carrier transport, still requires much more investigation. As a matter of fact, natural eumelanin is insoluble in common solvents and this has posed a challenge in film fabrication to study its physicochemical properties [124].

2.2.2 Electrical conduction in eumelanin

The electrical conducting behavior of eumelanin was reported for the first time in the 70s by McGinness *et al.* [125] after their observations of electrical resistive switching in both hydrated synthetic and natural pellets of eumelanin while no switching was observed dried samples. They suggested eumelanin as an organic amorphous semiconductor based on the modified dielectric constant model in which absorbed molecules by a biomaterial increase its local dielectric constant, which in turn lowers the activation energy for the charge carrier transport and thus the threshold switch voltage [126]. The amorphous semiconductor model was also supported by the broadband UV-Visible absorption spectrum which reflects a peculiar density of electronic states in the organic pigment [127-129].

Resistive switching (RS) is the property exhibited by some materials to reversibly change their electrical resistivity between different stable states, i.e., between a low resistance (conductive) state and a high resistance (non-conductive) state, under the effect of specific electric fields [130]. The physical origin of the mechanism behind resistive switching has been ascribed to various physical processes for different materials, which can be related to metal contact-material interface or bulk effects. These include the change in the Schottky barrier height (or width) by trapped charge carriers at the interface states [131], migration of oxygen vacancies [132], oxygen ions exchange at the interface with electrodes (typically in oxide-based heterostructures) [133, 134], conductive

metallic filaments and ionic space charge limited conduction (SCLC) filaments that can be turned off when a low voltage is applied [135-137], electronic phase transition from Mott insulator to metallic-like state [138], polaronic hopping-based resistive switching [139-141]. For eumelanin, we do not know which of these mechanisms is involved in its electrical conduction.

Further experimental studies conducted by Mostert et al. [19, 142, 143] demonstrated that the conductivity of wet synthetic eumelanin is governed by the comproportionation⁴ equilibrium reaction between the hydroquinone (HQ) and quinone (QI) groups through which absorbed water molecules generate mobile electrons (semiquinone free radicals SQ^-) and protons (H_3O^+) (see Figure 2.4). They proposed a mixed protonic-electron conductor where protons diffuse through a hydrated matrix by Grotthuss hopping mechanism⁵ [18, 19, 144]. However, the authors did not discuss the mechanism of the electronic transport contribution.

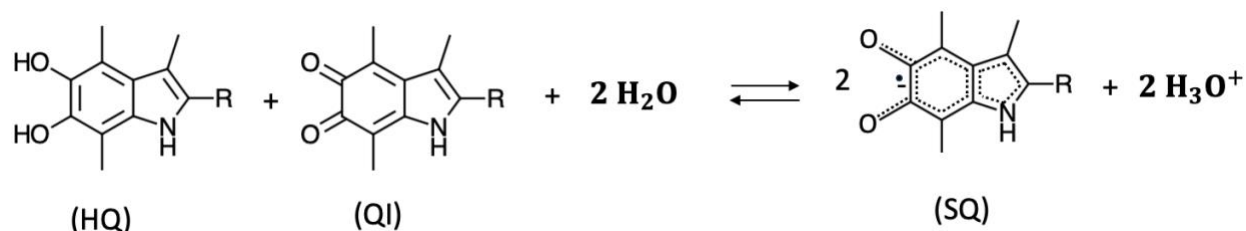


Figure 2.4 A scheme of comproportionation reaction regulating the concentration of the hydroquinone, semiquinone and quinone forms of eumelanin. In the presence of water, hydroquinone and quinone react to form hydronium ions (protons) and semiquinone free radicals (mobile electrons) (R represents H in DHI and COOH in DHICA) [19].

The mixed conductivity has also been confirmed by Wünsche et al., in their study where they considered samples of synthetic eumelanin (Sigma Aldrich) suspensions in dimethyl sulfoxide spin-coated on SiO_2/Si substrates [145]. It was pointed out a dominant proton transport over electronic transport at high relative humidity ($\sigma_H \sim 10^{-4} - 10^{-3} S cm^{-1}$ at 90 % RH). This was evidenced by a combination of Electrochemical Impedance Spectroscopy (EIS) and current-

⁴ A comproportionation reaction refers to a chemical reaction where one or more elements in different oxidation states combine to form a product in a single, intermediate oxidation state. The resulting product has a composition that is the average of the initial oxidation states of the reacting atoms, and the reaction is called a comproportionation equilibrium.

⁵ Grotthuss mechanism is based on the concept of a water chain conductive network inside the macromolecule promotes proton transport. In this process, a free proton or proton defect diffuses through the hydrogen bond network of water molecules or other hydrogen-bonded liquids through the formation and concomitant cleavage of covalent bonds which involves neighboring molecules.

voltage (I-V) characteristics measurements in a coplanar electrode structure using different electrodes: platinum (Pt) and palladium hydride (PdH_x : a non-blocking contact with respect to protons). Wünsche et al. proposed that electronic transport within eumelanin films could be constrained by proton migration, reversible redox processes, and the coupling of free (SQ) radicals [145].

With the aim of disentangling the electronic transport from the protonic contribution, Reali et al. [146] considered the same configuration of the device as McGinness et al. in the dry state. In their work, a predominant electronic conduction was noticed in dry melanin pellets while the wet pellets (19 % water per weight) exhibited a mixed conductivity with a predominant ionic (proton) conduction after switching. This time, the measured electronic conductivity of dry melanin could not be described in terms of a comproportionation equilibrium reaction as previously reported [19, 145]. Reali et al. suggested that the resistive switching observed in dry pellets occurs due to the electric field applied to the metal contacts, leading to the formation of a space charge layer at the interface between the metal and eumelanin. Increasing the applied voltage shifts the Fermi level towards the valence or conduction band, filling all the trap states at the interface, and leading to enhanced carrier injection. These findings suggested again an amorphous semiconducting character of eumelanin in which the Fermi surface is populated by unpaired electrons [125, 147].

We do not yet understand the mechanisms that control the concentration of electronic charge carriers and their mobility to confirm if eumelanin can be an organic semiconductor. Research is still needed to shed light on the mechanism behind mixed conductivity. Some of the fundamental questions about eumelanin are: How charge carriers are generated in mixed ionic electron eumelanin? How does the ion-electron coupling assist the charge carrier transport in this organic pigment?

To address these questions, one approach is to optimize the carrier injection process and/or conduction paths connecting the electrodes to collect a meaningful electrical response. It is in this context that this Ph.D. thesis focused on the choice of electrodes according to the eumelanin energy levels to define the metal contacts which minimize the Schottky barrier.

The morphological structure of eumelanin is also a major factor that impacts the conductivity as its poor solubility has always hindered the film fabrication for device characterization. Camus et al., have recently observed electronic transport in films flexographically printed from formulations

including Sepia and the (insulating) organic binder PVB (Polyvinyl butyral) [148], and the measured conductivity was as high as $10^{-3} \text{ S.cm}^{-1}$. Such values are typical for synthetic high-performance organic electronic polymers but quite uncommon for bio-sourced materials [149-151]. They proposed that inter-granular percolative transport in Sepia is enhanced due to the confining action of the PVB binder on the Sepia granules, whose proximity would induce the formation of conductive paths. The relation between that conductivity and the hierarchical structure of Sepia eumelanin is not understood. This prompted us to study the electrical conduction behaviour at the nanoscale, which was the second objective of this PhD thesis.

CHAPTER 3 EXPERIMENTAL METHODS

3.1 Spectroscopy

Locating the positions of the HOMO and LUMO energy levels in OSs is mostly carried out by ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). The UPS is used to characterize the valence band energy levels while IPES is a complementary technique to UPS to study the conduction band energy levels [152].

3.1.1 Ultraviolet photoemission spectroscopy

Photoemission spectroscopy (PES) involves shining electromagnetic radiation onto a sample to ionize its atoms or molecules. The fundamental principles of photoemission were clarified by Einstein's contributions to the understanding of the photoelectric effect. This phenomenon is noticeable as the surface of a material emits electrons when illuminated by electromagnetic radiation. In this process, light is considered in its particle-like behaviour, composed of "photons" i.e., packets of energy $h\nu$ ($h = 6.626 \times 10^{-34}$ J.s: Planck's constant and ν : radiation frequency). Once introduced in the sample, a photon interacts with the electron to which it will transfer the full of its energy $h\nu$. Each photoelectron is emitted with a kinetic energy E_K that depends on its binding energy BE with the nucleus atom as

$$E_K = \begin{cases} \text{meaningless,} & h\nu \leq E_I \\ h\nu - BE, & E_I \leq h\nu < \infty \end{cases} \quad (3.1)$$

where E_I is the ionization energy of the material as indicated in Chapter 1 [153].

As valence shell electrons are weakly bonded with the nucleus, they can be ejected with low-energy radiation, usually ultraviolet (UV) light. Hence, the valence band energy states in the solids are probed by the ultraviolet photoemission spectroscopy (UPS) technique that corresponds to photon energies $h\nu$ selected in the range of 10 - 45 eV (i.e., UV light). The UPS radiation source typically uses the Helium (He) discharge lamp providing two narrow-width emission lines: He I_α (21.2 eV) and He I_β (42.4 eV). It is a highly surface-sensitive technique due to the short inelastic mean free path of electrons in the material, which is defined as the average distance the electrons can travel between successive inelastic collisions [154]. As a result, the probed thickness is typically less than 4 nm from the surface.

The emitted photoelectrons are analyzed in the vacuum chamber to understand the chemical composition or the electronic energy states of the sample based on the number of counted electrons and their kinetic energy. Since the photoemission is anisotropic, electrostatic lenses are used to collect the photoelectrons which are then focused onto the entrance slit of the analyzer. Most of the photoemission instruments have a hemispherical analyzer with a negatively charged outer sphere and a positively charged inner sphere (see Figure 3.1 (a)). Once in the analyzer, their electron trajectory is bent as they are repulsed by the negative electrode and attracted by the positive electrode. If a constant voltage across the hemispherical electrodes is applied, higher kinetic electrons will still collide with the outer sphere. Similarly, low kinetic energy electrons will collide with the inner sphere. That means only electrons with a fixed energy will travel exactly through the exit slit path and reach the electron detector that counts them.

Therefore, the data acquisition of UPS spectra is mostly performed in fixed analyzer transmission (FAT) mode where the positive voltage electrode is varying to scan the kinetic energy of photoelectrons by retarding the measured values with respect to the range accepted by the analyzer called “pass energy” [155]. Finally, both the number of counted electrons and their corresponding kinetic energy are sent to the computer for data analysis. Briefly, the valence band spectrum is obtained based on the measured kinetic energy of the photoelectron E_K , from which one can deduce the wave vector of the photoelectron and the binding energy BE of each electron as $BE = h\nu - E_K - \phi$, where ϕ is the work function of the detector [156].

3.1.2 Inverse photoemission spectroscopy

The inverse photoemission spectroscopy (IPES) consists of probing the density of unoccupied states (above the Fermi level) using a monoenergetic electron beam (typically $E_k' \sim 5 - 15$ eV) in the sample. In the IPES electron gun, the barium oxide (BaO) cathode is indirectly heated to produce electrons by thermionic emission [157, 158]. Due to the low energy of the incident electrons, they will penetrate only a few atomic layers, which makes IPES a particularly surface-sensitive technique.

As they impinge on the sample, the electrons recombine randomly into all the unoccupied states below their kinetic energy. As a result, a Bremsstrahlung spectrum, associated with radiation decay of incident electrons into unoccupied energy levels, is generated [159, 160]. Essentially, this is like the process occurring in any X-ray gun where electrons from a filament bombard the X-ray cathode.

The obtained IPES spectrum cannot easily be measured and requires an expensive signal-attenuating UV monochromator. Detectors such as a Geiger Müller detector or a solid-state photomultiplier can be used to count the emitted photons without telling us much about their energies.

The technical approach is to operate in the “isochromat” mode using a bandpass photon detector (see Figure 3.1 (b)) which counts photons with a certain energy $h\nu' = E_{BP}$. This enables the precise counting of photons that stem exclusively from recombination within a specific, narrow range of states located in the conduction band. By modifying the acceleration potential in the electron gun, the kinetic energy E_K' can be varied, thereby shifting this energy window across the entire range of unoccupied states of interest. Finally, a photon count spectrum is generated, illustrating the relationship between photon count and binding energy BE' above the Fermi level (see Figure 3.1 (c)) based on the conservation energy law $BE' = E_K' - E_{BP}$ [157].

Despite their complex instrumentation, the UPS and IPES provide the advantage of studying the sample placed in ultrahigh vacuum ($10^{-10} - 10^{-8}$ mbar). This allows experiments on samples clean enough to give reproducible and meaningful results. In addition, it is relevant for locating the energy levels of semiconductors in a controlled atmosphere for samples sensitive to humidity and oxygen, which could alter the band structure as is the case in eumelanin film. In this Ph.D. thesis, the techniques allowed us to study, for the first time, the band structure of eumelanin in the solid state.

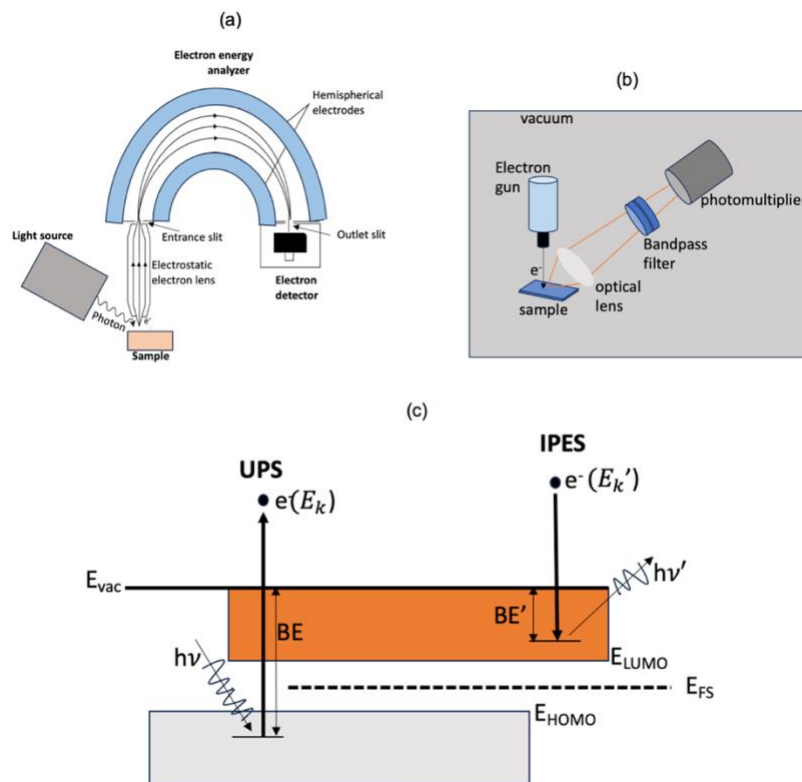


Figure 3.1 (a) Experimental setup of the direct photoemission spectroscopy adapted from [161]; (b) schematic diagram of inverse photoemission experimental configuration where photons are selected by a bandpass filter and analyzed in the photomultiplier, adapted from [162]. (c) Band diagram illustration electronic states associated with the UPS and IPES technique adapted from [163]

3.1.3 Samples for photoemission measurements

Due to the high surface sensitivity of the UPS and IPES techniques, materials of interest are required to be prepared with improved quality to avoid contamination impurities and states induced by disorder near the surface that tend to smear out the photoemission spectral features. The importance of sample preparation and control at the atomic/molecular level is indeed not restricted to photoemission in modern materials research.

In this Ph.D. thesis, UPS-IPES studies were feasible on samples fabricated considering powders of eumelanin building blocks, i.e., DHI (5,6-dihydroxyindole) and DHICA (5,6-dihydroxyindole-2-carboxylic acid), which were synthesized in chemically controlled pathways as reported in the literature [164]. The synthesis was done by our collaborator at the University of Napoli “Federico II”, Naples (Italy) who contributed to this project with his expertise in the synthesis of eumelanin. The powders were enclosed in sample holders with an N_2 atmosphere at the Naples synthesis

laboratory to prevent chemical degradation and then sent to Polytechnique Montreal and Dalhousie University for sample preparation and characterization. Upon arrival, the powders were stored in a freezer at approximately -20°C, prior to solution processing and/ or film deposition. However, we are aware that we do not have certainty about the aging time of powders from synthesis to sample preparation which might impact the morphological and electronic structure. This is beyond the scope of this Ph.D. thesis and a study may be needed in the future to clarify it.

Both solution spin-coating and vacuum deposition were adopted to fabricate eumelanin-based films. We are employing the word "film" as expected for simplicity. However, the terminology might be less appropriate as the degree of polymerization or the range of molecular self-assembly distance of eumelanin is not well understood. One could remain far from achieving a substrate coating with a few nanometers to several micrometers.

For solution processing, the DHI and DHICA-powders were dissolved in anhydrous methanol and ethyl acetate (1:1 v/v) to form 2 mg/mL mixture solutions. A solution volume of 30 μ L was cast onto the pre-cleaned substrate. Spin coating on 1 cm $\times$ 1 cm ITO substrates (Indium tin oxide) at 2000 rpm for 30 seconds was performed within a controlled atmosphere (N_2 glovebox, O_2 and H_2O < 5 ppm). Prior to deposition, the substrates were cleaned sequentially in an ultrasonic bath at 40 kHz with different solvents: deionized water for 5 minutes, isopropanol (IPA) for 15 min, acetone for 15 min and again IPA for 15 min. After ultrasonic bath cleaning, the nitrogen gun was used to dry the substrates, which were afterwards exposed to UV-ozone treatment for 15 minutes to remove residual solvent or any other organic contaminants.

The solid-state formation of the resulting (spin-coated) DHI and DHICA-based solutions was carried out under different atmospheres. Some samples underwent ammonia exposure to follow a protocol reported in literature [165], also called "ammonia-induced solid-state polymerization (AISSP)" for 72 hours. The rest of the samples were maintained within the glovebox to minimize contact with oxygen or moisture for the same duration. Note that all the solution-processed samples were inserted with tape in a KF-40 tube inside the N_2 glove box at Polytechnique Montréal (Canada) and shipped to the University of Dalhousie (Halifax, Canada) to ensure minimum contact with the ambient atmosphere during transportation.

For vacuum deposition, DHI and DHICA powders were thermally evaporated using a crosspiece evaporator in a vacuum, i.e., at a pressure of 10^{-8} mbar. The targeted thickness of the organic layer

was set to 10 nm using a quartz microbalance. After deposition, samples were left in the evaporation chamber for an hour, and subsequently, moved to the analysis chamber for UPS and IPES measurements.

The ultraviolet photoemission spectroscopy data were collected in a vacuum chamber (10^{-8} mbar) using a hemispherical energy analyzer (Phoibos 150, SPECS Group) in fixed analyzer transmission mode. The ultraviolet radiation was provided by a helium discharge lamp, with a differential pumping system where the emission line He I α (21.22 eV) was chosen for all the UPS spectra. IPES was employed with the Erdman-Zipf electron gun for thermionic emission. Photons were collected in isochromat mode using a band-pass photon detector. For the number of scans, IPES scans were repeated 10 times with an integration time of 1 s for each energy step (0.05 eV). UPS scans are similar, the step size is 0.01 eV, and the signal collection is 0.1 s where the number of scans performed is 5. One can think of it like a camera where we use a combination of duration along with scans (how long the “shutter” is open). Since luminosity is so large for UPS, fewer scans are required when compared to IPES.

To ensure reproducibility, four samples were measured for each type of sample of the solution-processed films (DHI, DHICA, AISSP-DHI, AISSP-DHICA) and their spectra were consistent. UPS and IPES measurements on evaporated DHI and DHICA films were performed on two samples for both evap-DHI and evap-DHICA, and the measurement was repeated 3 times. Note that we tried to restrict the time of permanence inside the deposition chamber to avoid contamination.

3.2 Microscopy

3.2.1 Atomic force microscopy

Developed in the 80s, Atomic Force Microscopy (AFM) is a prominent scanning probe method extensively applied in various research fields such as materials science, nanotechnology, biology, and surface chemistry. It enables studying matter through imaging, manipulation, and measuring the size of the nano- and microstructures to explore the structure-property relationship [166].

Atomic force microscopy relies on sensing the interaction forces acting on a sharp tip mounted on the microcantilever by raster scanning the sample surface performed by a piezoelectric actuator with a sub-angstrom accuracy [167]. These interactions are basically weak van der Waals forces

which can be attractive due to dipole-dipole interactions between atoms or molecules acting at the distance typically $r < 10$ nm or repulsive due to the overlapping of electronic clouds when the tip is in contact with the surface ($r < 1$ nm). By approaching the surface, the cantilever is sufficiently flexible with a low spring constant ($\sim 0.1 - 10 \text{ Nm}^{-1}$), enabling a force sensitivity as low as 10^{-12} N [168].

The most used AFM imaging modes are static contact mode (CM) and amplitude-modulation intermittent mode, which is commonly called “tapping mode” (TM). In contact scanning mode, the tip gently touches the sample surface interacting with a repulsive force and the cantilever is vertically deflected by changes in the surface topography [169]. In tapping mode, the attractive regime is the dominant one as the cantilever remains constantly oscillating with an amplitude of 20 - 100 nm, which is decreased by a repulsive force when the tip contacts the sample [167, 168].

The choice of operating mode is often based on the nanomechanical properties of the sample to be analyzed. Briefly, imaging tapping mode is suitable for a wide range of samples including soft or biological samples which can be easily damaged or detached from the substrate by the tip.

Depending on the operating mode, the cantilever deflection (CM) or oscillation (TM) is detected using a laser beam pointing at the back surface of the cantilever directly above the tip and gets reflected towards the position-sensitive photodetector (PSPD), which afterwards amplifies the deflection (or oscillation) signal [170]. Each deflection or oscillation of the cantilever moves the laser spot on the photodetector to a new location. This in turn will generate an error signal with respect to a fixed value of interaction force between the probe tip and the sample, prior defined by the AFM operator as a setpoint. Most scanning probe microscopes operate with a feedback circuit controller that compares the setpoint and real-time signal to minimize the error by applying a voltage to the piezoelectric scanner to adjust the tip-sample distance at a fixed value (See the experimental configuration in the Figure 3.2).

The overall feedback signals, corresponding to the height variation of the surface topography at each pixel point in a 2D matrix, are recorded to construct an AFM image. AFM images are usually presented with a coloured bar gradually specifying low and high topographic features. The analysis of the AFM images enables to study of the nanostructures of the material by evaluating their shape, height, depth, and lateral dimension (width).

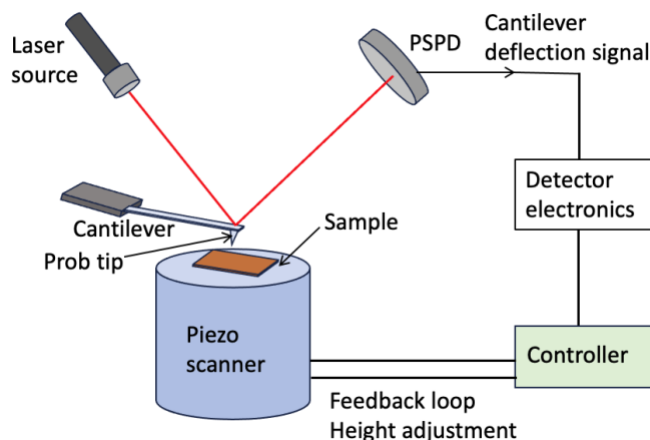


Figure 3.2. Experimental configuration of AFM, adapted from [168]

The spatial resolution of AFM is a function of the tip geometry and size, as well as the capability of feedback control of the interaction between the tip and the sample [171]. The AFM lateral resolution (i.e., the minimum measurable distance between two distinct points) is limited by the scanning probe tip. A tip with a high aspect ratio, i.e., characterized by a small radius curvature at the area contacting the sample, will easily deconvolute the profile of two adjacent spikes, giving rise to high resolution. Current commercial AFM cantilever-tips, which are typically micro-etched silicon sometimes coated with a metal, can provide a lateral resolution of around 1 nm [172].

On the other hand, AFM vertical resolution (AFM sensitivity), defined as the minimum step height detectable as two levels, is more related to system noise arising from the z-scanner, the electronic and optical detection systems of the microscope, acoustic and external mechanical vibrations, and thermal noise sources [168]. Therefore, the AFM instruments are always installed such that the measurements are isolated from all environmental effects that might couple to cantilever motions and induce artifacts. The AFM can be achieved down to the sub-nanometer level [173].

Several AFM advantages include the operation in a vacuum, air, and liquid as well as in-situ and/or temperature-controlled measurements allowing the characterization of various samples such as conductors, semiconductors, insulators, nanocomposites, polymers, and biological macromolecules [174, 175]. In addition, advances in AFM-derivative imaging modes enable nanoscale exploitation of spatial variations of mechanical, electrical, magnetic, chemical, tribological and thermal properties on the sample surface [176, 177].

3.2.2 Conductive atomic force microscopy

Conductive Atomic Force Microscopy (C-AFM) is an AFM technique applicable to conductive materials including metals, conductive polymers, conductive biomaterials, and nanostructured semiconductors for measuring a nanoscale electrical response at each location in the AFM image [178]. It works in contact mode to map the surface topography while simultaneously applying a voltage between an electrically conductive probe tip and the sample substrate. However, the lateral movement of the tip in contact mode involves dragging forces that are not suitable for scanning soft or biological samples. As one of the objectives of this thesis on bio-sourced sepia eumelanin (made of granules), was to study its electrical properties at the nanoscale, C-AFM was performed in HybriD (HB) mode (NT-MDT Spectrum Instruments) as described in section 3.2.4.

Briefly, in Hybrid mode, the features of two standard contact and AM-tapping modes are combined. The oscillatory cycle of the probe is composed of alternating non-touching and touching parts, making it possible to sense local mechanical interactions and electromagnetic forces acting on the tip when a bias voltage is applied between the probe and sample substrate [179, 180]. The electric current is indeed measured in the touching part of the cycle by applying the bias probe and sample. During scanning, the probe is retracted from the sample while moving to the next pixel point, thereby reducing the lateral interaction between the tip and the sample. HB-AFM mode is a non-destructive method suitable for studying fragile, soft, and weakly adhered films on a substrate [181].

3.2.3 Preparation of eumelanin samples studied with atomic force microscopy

Extraction of Sepia. Raw cuttlefish ink (Stareef Seafood Boston, product of Spain) was purchased in a Montreal fish market. Sepia powder was extracted using a previously reported extraction protocol [148, 182]. Briefly, 300 g of raw ink was suspended in 500 mL of HCl (2 M, Acros Organics). The suspension was stirred at room temperature for 24 hours, sequentially centrifuged (Allegra X-30R centrifuge, Beckman Coulter) and dispersed as follows: three times with HCl (0.5 M), once with de-ionized (DI) water, once with a buffer solution (0.02 %v/v of monobasic sodium phosphate (200 mM, Sigma Aldrich), 32.49 %v/v of dibasic sodium phosphate (200 mM, Sigma Aldrich) and 67.49 %v/v of DI water), once with ethanol (Sigma Aldrich), once with DI water and finally once with ethyl acetate (Sigma Aldrich), for a total of 10 steps. To remove excess ethyl acetate after centrifugation, the solid was rinsed, dispersed and centrifuged four times with DI

water. Each centrifugation step was performed at 10,000 rpm at 5 °C for different duration times (15 min for HCl 2 M, HCl 0.5 M, ethanol, and ethyl acetate, 25 min for DI water and the buffer solution). Finally, the extracted powders were lyophilized for 24 hours at -80 °C to remove excess water. Fine black Sepia eumelanin powders were obtained and manually ground to break large agglomerates. This extraction procedure provided 30 to 35 g of fine powders from 300 g of initial raw ink.

Sepia formulated ink. The preparation of the ink formulation was inspired by the formulation reported in [148], where the ink consisted of a blend of 64.8% w/w of 1-propanol (Sigma Aldrich), 19.1% w/w of Sepia powder, 11.4% w/w of Polyvinyl-butylal (PVB, B-30HH, MOWITAL®), 4.4% w/w of 1-methoxy-2-propanol (Sigma Aldrich) and 0.3% w/w of TEGO® Wet KL 245 polyether siloxane copolymer (Evonik).

The PVB is a binder used to hold the Sepia granules together and act as a film-forming agent. It helps to provide adhesion, durability, and mechanical strength to the film. 1-propanol is a solvent that serves as a dispersion medium for the ink formulation. It is selected based on the compatibility with the solid particles and their desired interaction with the substrate. The other compound (TEGO®) is a surfactant used to improve film spreading. These compounds do not modify the structure of sepia granules.

1-propanol and PVB were mechanically stirred at 600 rpm for 20 min. Afterwards, Sepia eumelanin was gradually added and mixed for 24 hours at 2,750 rpm in an attritor consisting of a high-rotation speed disk and zirconium oxide beads with a diameter of 1 mm, in a cooled vessel. The ink (with Sepia powder to PVB mass ratio is 62/38 %w/w) was obtained by adding 1-methoxy-2-propanol and TEGO® Wet KL 245. Differently from [148], in this work, the Sepia powder/PVB ratio was finally adjusted to 92/8 %w/w by adding Sepia powders to the 62/38 %w/w ink.

Preparation of substrates and samples. Two sets of samples were prepared, using Sepia powder and Sepia formulated ink (92/8 %w/w, Table S1). The powder was drop-cast from an ethanol suspension whereas the formulated ink was spin-coated (6,000 rpm, 40s) on gold-coated SiO₂ substrates (40 nm-thick Au, e-beam deposited on wet thermal oxide grown on the polished front side of a (1-0-0) Si wafer).

3.2.4 AFM and C-AFM measurements

The AFM images were acquired using the NTEGRA SPM system (NT-MDT Spectrum Instruments) in scanning by the sample configuration equipped with active anti-vibration protection. AFM (topography) images were collected in amplitude modulation (AM) mode. C-AFM images were collected in HybriD (HD) mode by applying 2 V between the gold substrate coated with the film and the Pt-coated AFM probe (with a nominal tip radius of about 35 nm). The c-AFM technique requires the mechanical stability of the material studied upon scanning the conductive tip. We therefore used a binder to enhance the adhesion and stability of the Sepia melanin granules on the gold-coated SiO₂ substrate. Table 3.1 provides details on samples characterized by AFM and C-AFM.

Table 3.1 Characteristics of the samples measured by AFM for this study. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) Nanoscale Adv., 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

Sample	AFM characterization	Deposition method	Scanned area	Figure
Sample 1	AFM (Topography)	Spin coating (Sepia eumelanin-PVB ink)	2.5 μm x 2.5 μm 1 μm x 1 μm 600 nm x 600 nm	-
Sample 2		Spin coating (Sepia eumelanin-PVB ink)	700 nm x 700 nm 700 nm x 700 nm	-
Sample 3		Spin coating (Sepia eumelanin-PVB ink)	3 μm x 3 μm 1 μm x 1 μm	Figure 5.2 (a) Figure 5.2 (b)
Sample 4		Spin coating (Sepia eumelanin-PVB ink)	20 μm x 20 μm 5 μm x 5 μm 1.5 μm x 1.5 μm 700 nm x 700 nm	-

Sample 5		Spin coating (Sepia eumelanin-PVB ink)	20 μm x 20 μm 5 μm x 5 μm	-
Sample 6		Spin coating (Sepia eumelanin-PVB ink)	2 μm x 2 μm 500 nm x 500 nm	-
Sample 7		Drop casting (Extracted Sepia eumelanin)	2 μm x 2 μm 1.2 μm x 1.2 μm 400 nm x 400 nm	-
Sample 1	c-AFM	Spin coating (Sepia eumelanin-PVB ink)	2.5 μm x 2.5 μm 1 μm x 1 μm 600 nm x 600 nm	-
Sample 2		Spin coating (Sepia eumelanin-PVB ink)	700 nm x 700 nm 700 nm x 700 nm	-
Sample 3		Spin coating (Sepia eumelanin-PVB ink)	900 nm x 900 nm	Figure 5.2 (c)

CHAPTER 4 BAND STRUCTURE IN EUMELANIN FILMS

This chapter covered our study on the energy band structure of eumelanin in solid-state, aiming to fulfill our first objective, i.e., locating the HOMO and LUMO energy levels for exploring the charge carrier injection mechanism in electronic device configurations. We refer the reader to see the details of the experimental methodology described in Chapter 3.

Briefly, the as-prepared eumelanin films were named according to atmosphere exposure after deposition: (i) “DHI” and “DHICA” for solution-spin-coated eumelanin suspension, afterwards exposed in a controlled oxygen and humidity atmosphere (N_2 glovebox: O_2 and H_2O levels < 5 ppm) (ii) “AISSP-DHI” and “AISSP-DHICA” for ammonia solid-state-induced polymerized eumelanin after spin-coating as elaborated in literature [184-187] and (iii) “Evap-DHI” and “Evap-DHICA” for thermally evaporated monomers formed in vacuum ($\sim 10^{-8}$ mbar).

We also recall that the UPS and IPES measurements, the results of which are mainly discussed in this study, were carried out at Dalhousie University (Canada) in collaboration with the research group of Professor Ian Hill.

4.1 Location of the HOMO and LUMO energy levels

4.1.1 Data analysis

UPS and IPES spectra of OSs are usually modelled assuming a Gaussian distribution of photoelectron counts from each energy level within the band structure [188-190]. With a metal sample, the Fermi level is quite marked and easy to detect (with a very well-known analytic expression) and so the relative uncertainties are quite small. For semiconductors, on the other hand, the emerging states are difficult to separate from the background. The band gap corresponds to the difference in energy level between the onset of the HOMO/LUMO rather than the peak feature. We used the linear extrapolation method along the steepest point of the HOMO/LUMO feature intersecting with a linear extrapolation along the background. The band edges are considered as the "onsets" of the frontier orbitals at the emerging spectral features corresponding to the HOMO (E_{HOMO}) and the LUMO (E_{LUMO}) energy levels located relative to the Fermi energy level. This method is limited to how well the feature can be resolved, which requires quantifying the associated errors.

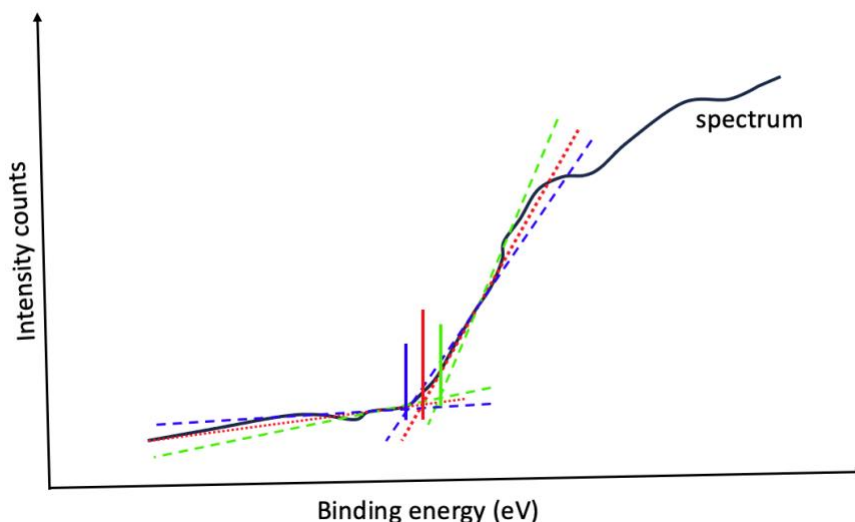


Figure 4.1. illustration on quantification of errors using the linear fits.

The uncertainties were determined by fitting best-fit lines, to the background and rising edge of the spectrum. Now, this is a subjective practice and so there are upper and lower bounds to what one would call "reasonable fits" and the central "best fit" illustrated in Figure 4.1. The best fit in this case is the central red fit with short-dashed lines, while lower and upper bounds are given by the blue and green long dashed lines, respectively. You can see how this procedure yields three intersection points, with the upper and lower being equidistant from the central point. Thus, the uncertainty is reported as the distance between these points.

For UPS, the spectral edges of the prepared DHI and DHICA-based films are quite sharp due to the strong HOMO feature against a very weak background, leading to a minimal difference between "maximum possible" and "minimum possible". This essentially minimized the uncertainty down to 0.05 eV. For IPES, the LUMO feature is unclear, and the background count rate is several orders of magnitude larger than UPS. LUMO level is estimated with a wider range of "reasonable fits" (i.e. much more noise), hence, the larger uncertainties. Propagation of errors will occur in the calculated band gap, but the IPES uncertainty is much larger that it dominates the UPS contribution.

The calculation of the ionization energy and electron affinity requires the location of the vacuum level E_{vac} . Thus, a silver (Ag) reference sample was used to calibrate the spectrometer by setting the Fermi level to zero binding energy. The procedure is easy since a metal like silver has the characteristic "Fermi step", clearly seen in the blue plot shown in Figure 4.2.

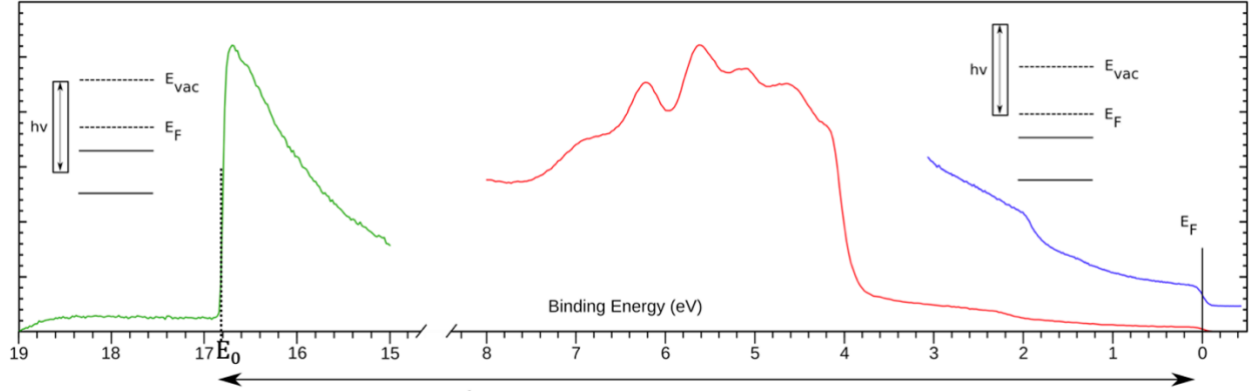


Figure 4.2. The energy scale that illustrates the setting of the binding energy of the fermi level at zero using the Ag reference and Helium light source (21.2 eV). In the UPS spectrum (red curve) for the material, the interesting features are referenced to the Fermi level. The green curve shows the onset electron emission corresponding to E_0 .

To know the position of E_{vac} , which varies with materials, we look for what is called "the secondary electron cutoff" E_0 here located at 16.8 eV with respect to the Fermi level (E_F). Essentially, at the point E_0 , the helium source is not strong enough to excite anything from the sample, including elastically scattered electrons right at the material surface. This is reflected in the band diagram where the excitation source is only able to reach the vacuum state. Thus, if we take the distance from this cut-off to the (already calibrated) Fermi energy, we were able to measure the work function of the metal (or equivalent interpretation for semiconductors/insulators), given as $\phi = h\nu - (E_0 - E_F) = 21.2 \text{ eV} - 16.8 \text{ eV} + 0.0 \text{ eV} = 4.4 \text{ eV}$, which is the expected value for silver. Thus, this gives the location of the vacuum level, which allows us to calculate the ionization energy for our samples, knowing the HOMO position relative to Fermi level. For IPES, we assume that the energy of the vacuum level is unchanged, and the electron affinity is measured following the same procedure. Then, the values of the ionization energy (E_I) and electron affinities (χ_E) were deduced using equations (4.1) and (4.2).

$$E_I = h\nu - (E_0 - E_{HOMO}) \quad (4.1)$$

$$\chi_E = h\nu - (E_0 - E_{LUMO}) \quad (4.2)$$

4.2 Results and discussion

In Figure 4.3 (a), the band edges of spin coated DHI are located at $E_{HOMO} = 1.12 \pm 0.05 \text{ eV}$ and $E_{LUMO} = -0.6 \pm 0.3 \text{ eV}$, with respect the Fermi level. This corresponds to $E_I = 5.56 \pm$

0.05 eV and $\chi_E = 3.8 \pm 0.3$ eV. The results for all the samples are presented in Figure 4.3 and Table 4.1.

Table 4.1. HOMO and LUMO energy levels located with respect to the Fermi level, ionization energy (E_I) and electron affinity (χ_E), and transport energy gap. (Reproduced from [191] with permission of John Wiley and Sons).

Samples	HOMO (eV)	LUMO (eV)	E_I (eV)	χ_E (eV)	HOMO-LUMO gap (eV)
Evap. DHI	1.47 ± 0.05	0.0 ± 0.2	5.47 ± 0.05	4.0 ± 0.2	1.5 ± 0.2
Evap. DHICA	1.95 ± 0.05	0.0 ± 0.2	5.80 ± 0.10	3.9 ± 0.2	1.9 ± 0.2
DHI	1.12 ± 0.05	-0.6 ± 0.3	5.56 ± 0.05	3.8 ± 0.3	1.7 ± 0.3
DHICA	1.16 ± 0.05	-1.4 ± 0.5	5.61 ± 0.05	3.0 ± 0.5	2.5 ± 0.5
AISSP-DHI	1.09 ± 0.05	-1.0 ± 0.5	5.34 ± 0.05	3.2 ± 0.5	2.1 ± 0.5
AISSP-DHICA	1.20 ± 0.05	-1.6 ± 0.5	5.35 ± 0.05	2.5 ± 0.5	2.8 ± 0.5

4.2.1 The HOMO energy levels in solution-processed and thermally evaporated eumelanin films

In Figure (4.3 (a) and (b)), the HOMO peaks for DHI and DHICA are well-resolved in contrary to their AISSP counterparts (Figure 4.3 (c) and (d)). The lack of a clear gaussian peak in the UPS of the AISSP samples could be due to a few reasons. If one assumes a homogeneous sample, the integrated photoemission intensity depends on many factors expressed in equation (4.3) as described by Powell, C. [192]

$$I_i = N_i \sigma_i n_i T(E_K) \lambda_i(E_K) c. \quad (4.3)$$

where I_i : represents the total photoelectron intensity;

N_i : represents the atomic density of element I;

σ_i : denotes the photoionization cross-section (i.e., the probability per unit area that a photon with energy will ionize an atom or molecule);

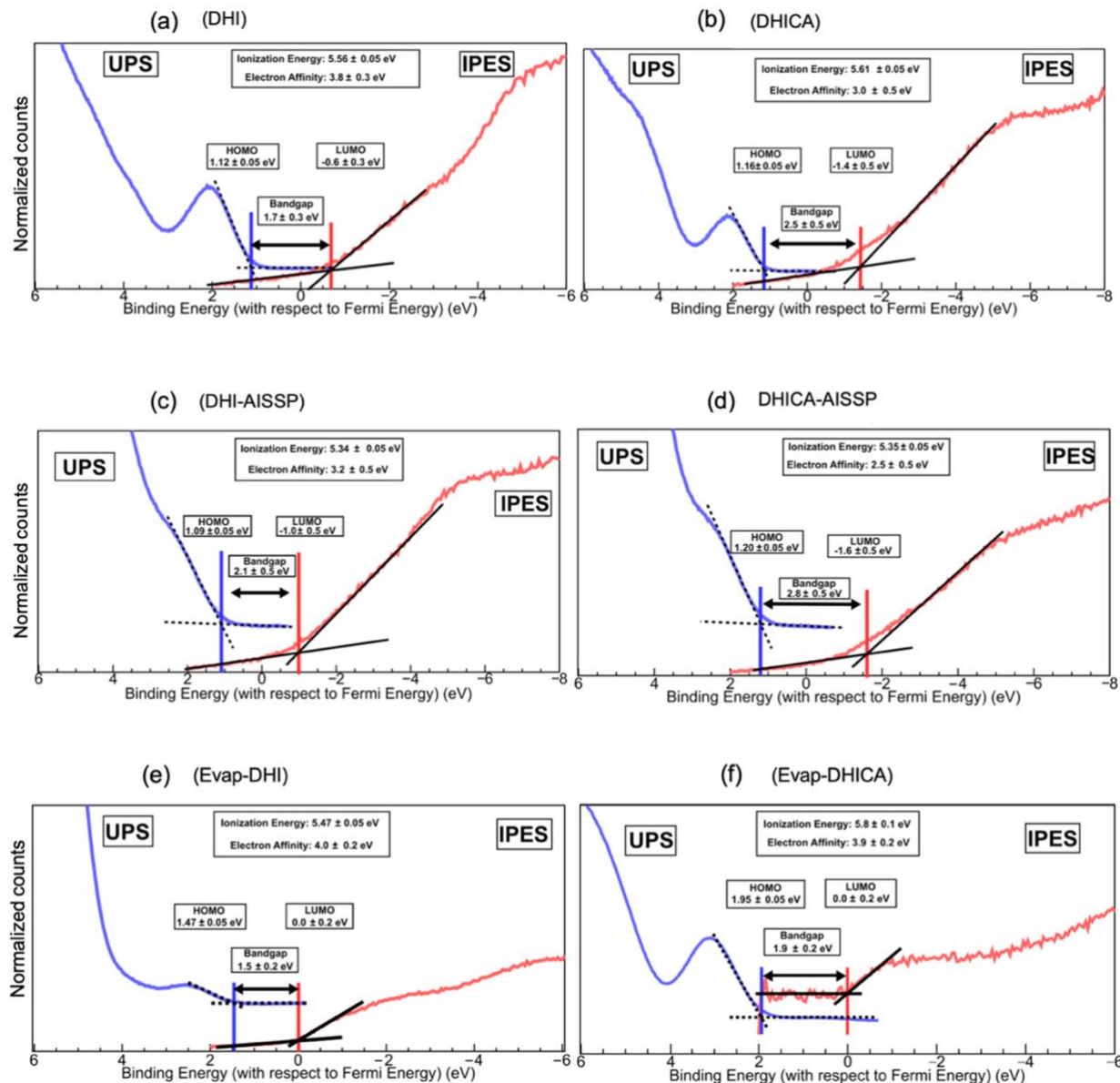


Figure 4.3. UPS (blue curve) and IPES (red curve) edge spectra of (a) DHI, (b) DHICA, (c) AISSP-DHI, (d) AISSP-DHICA, (e) Evap-DHI, and (f) Evap-DHICA films. Black dotted lines are the linear fit between the background noise and the emerging UPS and black solid lines are analogues for IPES spectra, to locate the HOMO and LUMO levels, respectively (Reproduced from [191] with permission of John Wiley and Sons).

n_i : the electron occupancy per cation;

$T(E_K)$: is the spectrometer's transmission function;

$\lambda_i(E_K)$: the electron escape depth, which varies with the photoelectron kinetic energy E_K ;

and the constant c is related to geometric factors [192, 193].

It is not straightforward to figure out which of those factors contributes significantly to the shape of the obtained spectra. The intensity ratio of the HOMO peak relative to the higher binding energy peaks ($I_{\text{HOMO}}/I_{\text{HBE}}$) impacts its resolution. Higher density of states and large photoionization cross-sections for those molecular orbitals at the used excitation energy (21.2 eV, in this case) [194, 195], will increase the ratio $I_{\text{HOMO}}/I_{\text{HBE}}$, making easier the resolution of the HOMO peak.

Although we did not explore a comparative study in terms of σ_i , N_i , and n_i , we propose the hypothesis that the HOMO peaks in AISSP samples appear as weaker shoulders on the higher binding energy features possibly due to the lower kinetic energy photoelectrons that are inelastically scattered within the sample before escaping into the vacuum. This increases the background signal that broadens the spectrum at higher binding energies [196]. In other words, films prepared following the polymerization under the atmosphere involving ammonia (and air) exposure (AISSP-DHI, AISSP-DHICA) feature a more structural disorder resulting from several pathways of the molecular bonding, packing or physical self-assembly.

On the other hand, the lower ionization energies of AISSP-DHI, AISSP-DHICA are attributable to extended occupied states. It is evident that the ammonia atmosphere is affecting the electronic structures of eumelanin. To the best of our knowledge, gaseous ammonia does not chemically react with DHI [184]. Furthermore, we can neither confirm nor exclude the possibility of extrinsic electrons induced by the atmosphere to molecular species of the films (i.e., chemical doping through the ambient humidity assuming role of humidity in the electrical conduction of eumelanin). According to previous studies, the ammonia atmosphere acts as a catalyst for oxidative polymerization from eumelanin building blocks [186]. One can tentatively explain that behavior by an improved degree of polymerization in AISSP, that led to enhanced π –orbitals overlapping. As a result this shifts the HOMO energy levels of AISSP films at lower binding energies [197, 198].

The low-intensity peak in Evap-DHI compared to Evap-DHICA can be attributed to the presence of -COOH groups in DHICA which led to differences in molecular packing under vacuum which generated the electronic states differently for the two monomers. All in all, since we were defining the “HOMO edge” as by the low binding energy edge of the peak, we were able to find this position, even in the case of the AISSP samples, where the gaussian peak is not as clearly

defined as we would like.

4.2.2 The LUMO energy levels in solution-processed and thermally evaporated eumelanin films

On the IPES side, which has much lower count rates (10,000x, at least) and lower energy resolution (10x worse) than UPS, the spectrum shape of the transfer function is dominated by the IPES detector. The low photon energy edge is defined by the photoionization threshold of the electron source, while the high energy edge is defined by the cut-off of the band-pass photodetector. The result is an asymmetric transfer function, with the lower energy edge slowly increasing (almost exponentially), and a much sharper high energy edge. This is what causes the long tail of intensity into the gap. It is a limitation of the IPES detector and not intensity counts within the gap. Consequently, the conduction band edges of DHICA, AISSP-DHI, and AISSP-DHICA films (see Figure 4.2.1 (b), (c), and (d)), were located with an approximate error of about 0.5 eV (which is large) associated with the LUMO level, leading to the same uncertainty in the deduced electron affinity and bandgap values.

The lower bandgap of all DHI-based films compared to their DHICA-based counterparts can be tentatively explained as arising from the long π - π stacking length of DHI-oligomer units than that DHICA [12]. A more extended π -electronic delocalization is expected to reduce the bandgap, as the size of bands is enlarged, thereby bringing the HOMO and LUMO levels towards each other [13]. For DHICA-based films, the twisting conformation and rotational disorder associated with DHICA oligoindoles that are prone to limit the π -conjugation could lead to narrower bands than in their DHI counterparts [94, 116]. On the other hand, the large uncertainty on the electron affinity value for AISSP-DHI did not allow a meaningful comparison of the energy gaps between DHI and AISSP-DHI samples based on the impact of the atmosphere.

For films deposited through thermal evaporation, the precision in IPES measurements was improved as the samples were prepared in UHV. However, there is an evident exception in the positioning of the LUMO levels, which are situated slightly above the Fermi level for thermally evaporated DHI and DHICA. This requires further studies to shed light on the mechanism associated with the noticeable shift in energy levels.

4.2.3 UV-visible spectroscopy

With the aim of studying the absorbance for further understanding of the optical excitation energies in comparison to the HOMO-LUMO gaps, we conducted UV-Vis spectroscopic analysis using the Agilent Cary 7000 UMA spectrophotometer in ambient conditions. For this purpose, samples were coated onto fused silica glass substrates (diameter: 1.4 cm, thickness: 1 mm, double-side polished, $T > 90\%$ in UV and visible regions). Spectral data for reflectance (R) and transmittance were acquired from the near-IR ($\lambda = 1000$ nm) to the ultraviolet range (up to $\lambda = 250$ nm). The absorbance (%A) was determined as $A = 100 - \%R - \%T$.

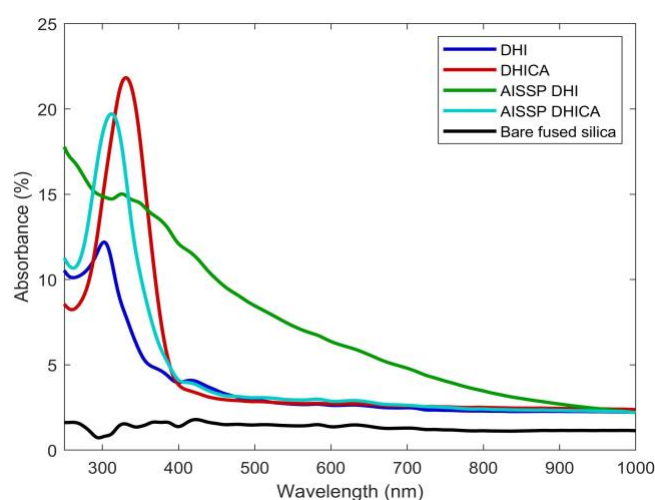


Figure 4.4 Total absorbance of spin-coated organic films deposited on fused silica substrates from solutions of mixed anhydrous methanol-ethyl acetate (1:1 (v/v), 2 mg/ml) solvent. (Reproduced from [191] with permission of John Wiley and Sons).

The results revealed that AISSP-DHI exhibits a broadband absorption spectrum in agreement with the natural eumelanin characteristics (see Figure 4.4). This shows the implications of ammonia in the step of oxidative polymerization which leads to supramolecular formation like that in natural pigment. On the other hand, the ammonia exposure on DHICA-based films does not show a significant effect on the optical absorbance since both DHICA and AISSP-DHICA as well as DHI exhibit preferred chromophore peaks within 300 - 350 nm corresponding to the energy in the range of 3.54 - 4.13 eV. However, this energy range is not consistent with optical bandgaps in the samples which should not exceed the HOMO-LUMO bandgap indicated in Table 4.1 [199]. On the other hand, the enhanced absorption towards UV regions is consistent the excitonic coupling introduced in the geometric disorder model discussed in section 2.2.1.

CHAPTER 5 SEPIA EUMELANIN: NANOSTRUCTURES AND ELECTRICAL PROPERTIES

5.1 Conductive AFM experiments

Following the high electrical conductivity of printed films Sepia-Polyvinyl Butyral (PVB) formulated ink observed by Camus et al. [200], in which charge carrier transport was described by the percolation model at a distance range of several microns, further studies were required to shed light on the implications of eumelanin structures. In this thesis, we studied the electrical conductivity of sepia with AFM and c-AFM aiming to elucidate the conduction behaviour at the nanoscale. Samples were prepared using the spin-coating technique from Sepia-PVB ink to ensure mechanical stability under direct interaction with the c-AFM tip (see details in Chapter 3 (experimental methods, Section 3.3)).

In the AFM images (Figures 5.1 (a) and (b)), the quasi-spherical granules are attributed to Sepia eumelanin and their contact is improved by the PVB binder as previously reported [200].

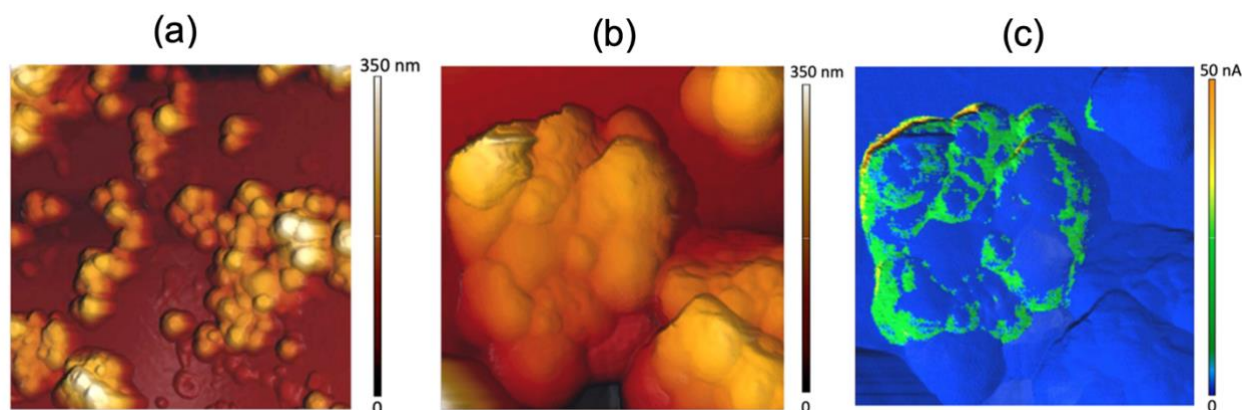


Figure 5.1 AFM images of Sepia-PVB films: (a) 3 μm x 3 μm -sized, (b) 1 μm x 1 μm -sized and (c) current image corresponding to the AFM image in (b). Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

The current overlaid on the topography in the c-AFM image (Figure 5.1 (c)) results in the establishment of conductive paths from the gold substrate through Sepia granules to the c-AFM tip. Several areas on granule surfaces are conductive, primarily located at the granule's boundaries, regions where the PVB binder is presumably not or less present. On the other hand, the inhomogeneous current distribution over the surface can be ascribed to the PVB insulating layer at

either the AFM probe- or gold-Sepia eumelanin interfaces. In addition, this may also be due to the unsuitable contact between such a non-uniform surface and the platinum-coated tip, for which the carrier injection energy barrier has not been quantified yet. These results evidenced, for the first time, the electrical response of Sepia eumelanin at the nanoscale. We then proceeded to characterize its nanostructures with AFM to shed light on the electrical properties.

5.2 Observation of the hierarchical structure

To study the structure of eumelanin at the nanoscale, the AFM was performed on the extracted sepia eumelanin powder drop cast on Au-SiO₂ substrates from ethanol (see the details in experimental methods, section 3.3). The analysis of the AFM data was carried out using the Image Analysis software from NT-MDT Spectrum Instruments.

Quasi-spherical granules are shown in high-resolution AFM images (see Figures 5.2 (a) and (b)). The size of granules was measured on granules with clear boundaries on the top surfaces. The diameters of these granules range between 120 and 300 nm as detailed in Table 5.1 and depicted in the histogram in Figure 5.2 (c).

Table 5.1. Diameters of granules measured from drop cast Sepia eumelanin. The average is calculated over granules with size in the considered interval. The associated errors are calculated standard deviations over the size ranges. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) Nanoscale Adv., 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

Range of measured Granules' diameters (nm)	Average diameter of granules (nm)	Frequency (%)
120 - 129	122 ± 4	2
140 - 149	143 ± 4	2
150 - 159	155 ± 7	12
160 - 169	166 ± 6	4
170 - 179	177 ± 12	8
180 - 189	183 ± 7	4

190 - 199	194 ± 4	6
200 - 209	204 ± 11	20
210 - 219	216 ± 7	10
220 - 229	223 ± 16	14
230 - 239	232 ± 12	6
240 - 249	244 ± 11	6
250 - 259	257 ± 12	4
290 - 300	291 ± 10	2

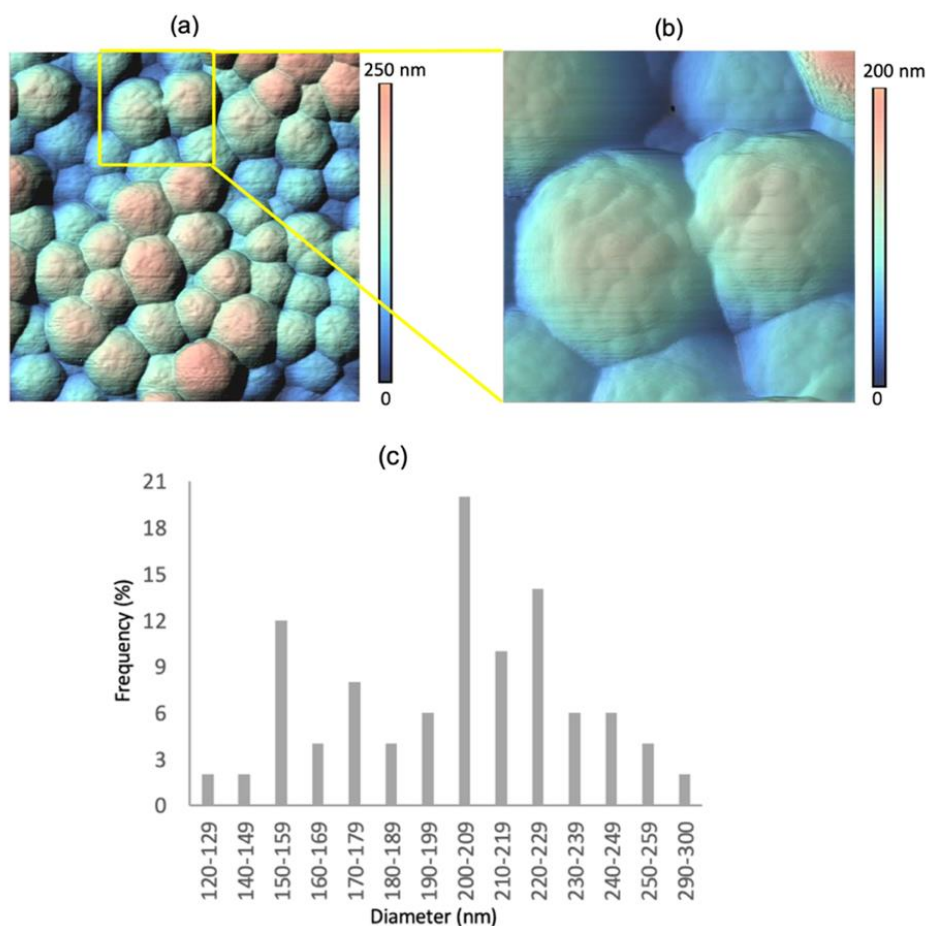


Figure 5.2 (a) A 1.2 μm x 1.2 μm AFM image of Sepia drop cast on the gold-coated SiO₂ and (b) a 400 nm x 400 nm high magnification AFM image that corresponds to the marked square in (a). (c) A histogram illustrating the size distribution of the Sepia granules. Diameters of granules measured from drop cast Sepia eumelanin. The average is calculated over granules with size in the considered interval. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

Each granule surface has protrusions, thus suggesting the existence of particle-like subunits within the granule. These observations are consistent with the findings from previous studies reported in the literature [118-121, 123].

The sizes of protrusions were measured from the local height profile on the granule surface. The Python software was used to plot and fit the heights, assuming spherical granules. The profile of each line in Figure 5.3 (a) corresponds to an arc of a circle that is part of the sphere. This circle includes points marking the lowest topographic parts of the protrusions, shown with blue cross-points in Figure 5.3 (b). The data fitting was done using the equation (5.1)

$$(x - x_0)^2 + (y - y_0)^2 = r^2 \quad (5.1)$$

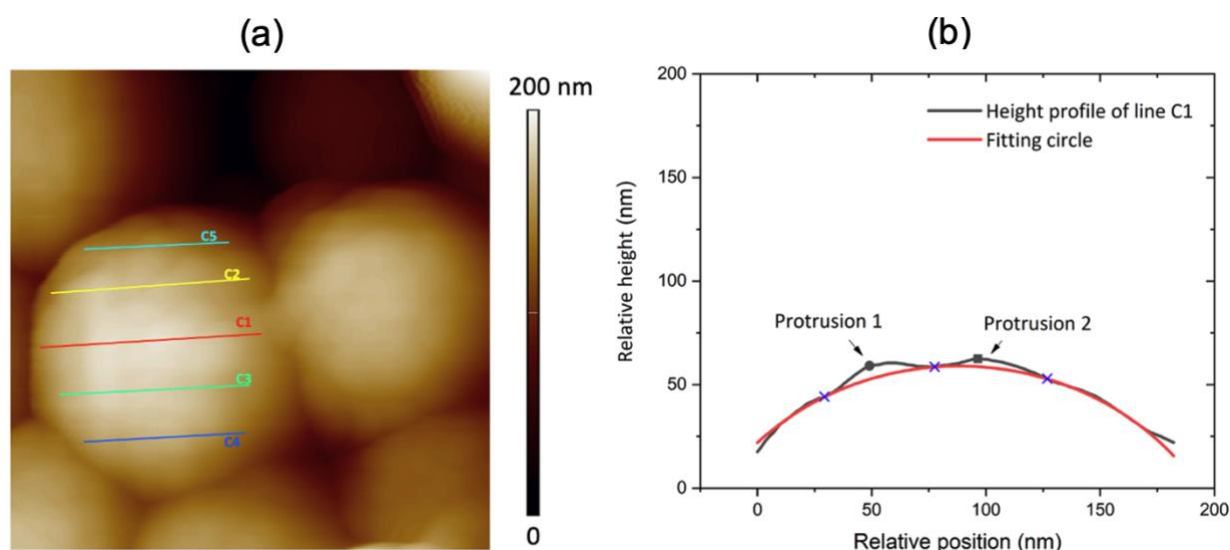


Figure 5.3 (a) 400 nm x 400 nm AFM image of Sepia drop cast on Au-on-SiO₂, (b) Relative height of the surface profile associated with line C1 on the granule in (a). Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

In equation (5.1), x and y represent the relative positions of each point on the line, while (x_0, y_0) represent the coordinates of the center of the fitting circle, and r denotes its radius. The height of each protrusion was then deduced as the distance from its highest point to the center of the fitting circle (x_0, y_0) , from which we subtracted the radius r . The width of the protrusion was determined at the midpoint of its height, namely the Full Width at Half Maximum (FWHM).

Table 5.2 Protrusions' heights over the surfaces of sepia granules, indicating a size range of the particle-like subunits. The associated errors are calculated standard deviations over the size ranges. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

Range of protrusions heights (nm)	Average height (nm)	Frequency (%)
1.0-1.9	1.5 ± 0.3	27.56

2.0-2.9	2.4 ± 0.3	35.89
3.0-3.9	3.4 ± 0.3	17.95
4.0-4.9	4.5 ± 0.4	6.41
5.0-5.9	5.3 ± 0.3	6.41
6.0-6.9	6.7 ± 0.3	2.56
7.0-7.9	7.5 ± 0.3	3.20

Table 5.3 Protrusions' widths over the surfaces of sepia granules, indicating a size range of the particle-like subunits. The associated errors are calculated standard deviations over the size ranges. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, 5, 5295-5300) with permission of Royal Society of Chemistry.

Range of protrusions width (nm)	Average width (nm)	Frequency (%)
6.0-10.9	9.1 ± 1.3	6.28
11.0-20.9	15.6 ± 2.5	57.14
21.0-30.9	25.3 ± 3.0	22.29
31.0-40.9	35.3 ± 3.7	7.00

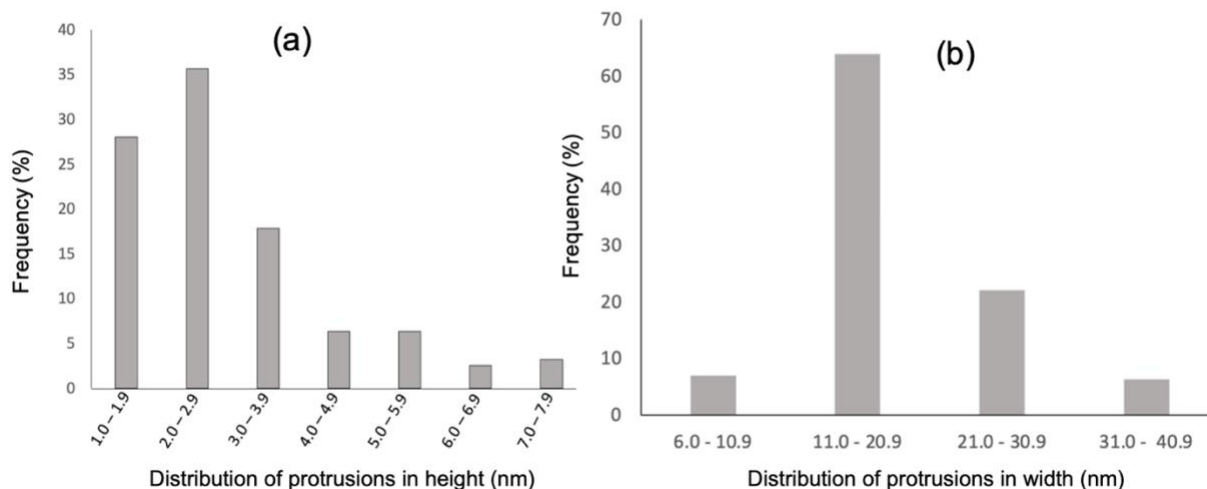


Figure 5.4 Size distribution in height (a) and width (b), of protrusions measured on sepia eumelanin granules. Reproduced from [183] (DOI: 10.1039/D3NA00355H (Paper) *Nanoscale Adv.*, 2023, **5**, 5295-5300) with permission of Royal Society of Chemistry.

Details on the measured values are given in Table 5.2 and Table 5.3. Our results indicate that protrusion heights range between 1.0 and 7.9 nm and most sizes are measured between 1.0 and 3.9 nm (see Figure 5.4 (a)). As for the widths, they vary from 6.0 to 40.9 nm, with a predominant size (64 %) between 11.0 and 20.9 nm, (see Figure 5.4 (b)), The overall average values for width and height were 18.5 ± 6.4 nm and 3.0 ± 1.6 nm, respectively.

Considering these dimensions, protrusions are consistent with small particles (10-15 nm) previously reported [118-121, 201]. Thus, our results support the hierarchical model elucidating the supramolecular buildup of Sepia nanostructures. However, the results obtained from AFM do not allow us to understand the internal structure of each granule. According to observations by Cheng, J. et al. in their XRD experiments, the local supramolecular arrangement of eumelanin features a paracrystalline structure [111, 112]. This is also in agreement with the coexistence of planar structures and twisted molecular conformation features, based on molecular interactions such as π - π stacking, cation- π interaction and hydrogen bonding [202-204].

CHAPTER 6 GENERAL DISCUSSION

In this thesis, we studied eumelanin biopigment owing to its properties, including the mixed ionic-electronic conductivity, redox behaviour, and the ability to provide photoprotection and antioxidant effects in living tissues. In addition, eumelanin is edible, biocompatible, and potentially biodegradable.

One of the requirements to develop high-performance organic electronic devices based on eumelanin is the characterization of the band structure in film forms. This is important for improving the charge carrier injection to achieve a high electrical conductivity as we discussed in Chapter 1 (section 1.3). Furthermore, studying the structure of eumelanin at both nano and micro scales is of utmost importance to understand the physical and chemical properties associated with the charge carrier transport, etc. In this chapter, we give a general discussion on the results presented in chapters 4 and 5 which covered the study on the band structure of eumelanin model films and the electrical response of nanostructures of (natural) *Sepia* eumelanin, respectively.

6.1 Energy levels and film processing routes

The HOMO and LUMO energy levels are measurable for DHI- and DHICA-films prepared by solution spin coating and thermal evaporation. We observed differences in the locations of the band edges concerning different monomers (i.e., DHI vs DHICA) and different atmospheres (i.e., ammonia-enriched atmosphere, N₂ atmosphere in the glovebox, and vacuum). The molecular structure of the DHI/DHICA monomers is a factor that is involved in the band structure since the DHI oligomers are more likely to form $\pi - \pi$ stacked planar structures and DHICA oligomers are associated with twisted structures that lead to rotational disorder. Thus, the HOMO energy levels are located at lower binding energies in DHI-films than in DHICA-films. We can tentatively attribute a more electron delocalization to DHI-films [205], which exhibited a lower HOMO-LUMO gap after deposition in vacuum.

The energy levels of the highest occupied molecular orbitals for polymerized samples under ammonia vapour (AISSP-DHI, AISSP-DHICA) were located with low-resolution of HOMO peaks from UPS spectra. This is due to structural disorder induced by polymerization under the ammonia, i.e., an atmosphere in which the ambient air was not sufficiently controlled. As

discussed in section 1.2 and illustrated in figure 1.2 (Chapter 1), one could expect a lower HOMO-LUMO gap in AISSP-DHI and AISSP-DHICA samples. However, large errors associated with LUMO energy levels did not allow us to make a conclusive comparison. Furthermore, this might not be the case since several physical interactions can lead to aggregated structures that limit the electron delocalization along the molecular chain. For DHICA samples, the structural disorder can originate from several degrees of freedom associated with the monomer units such as rotational disorder around covalent bonds, nonbonded intra- and interchain H-bonds, interrupted interchain π -stacking, and the oxidation of DHICA units when the polymerization reaches ~ 10 repeating units which also induces disorder [205, 206].

For the as-prepared films, the HOMO edges are determined by ultraviolet photoemission spectroscopy (UPS), with ionization energies (E_I) in the range of 5.34 - 5.80 eV. If we assume clean surface metal work functions, the candidate metal electrodes to study the hole injection mechanism in device configuration seem to be Pt(111): 5.91 eV, Pt(110): 5.53 eV, Pt(100): 5.75 eV, Pd (100): 5.48 eV, Pd(111): 5.53 eV, and Au(111): 5.33 eV [207]. The electronic affinity (χ_E) is measurable for 3 samples which were exposed in a controlled atmosphere (glove box, vacuum) namely DHI ($\chi_E = 3.80$ eV), Evap-DHI ($\chi_E = 4.0$ eV), and Evap-DHICA ($\chi_E = 3.9$ eV). We propose Ag (100): 4.10 eV and Al (110): 4.23 eV to explore the electron injection mechanism considering the protection from electrode oxidation (i.e., storage in a controlled oxygen atmosphere and electrical characterization under vacuum conditions).

These present results demonstrated that the surrounding atmosphere in sample processing has an impact on the electronic energy levels of eumelanin films. This study paved the way for defining contact electrodes that minimize the charge injection barrier and therefore charge carrier transport mechanisms in eumelanin-based devices.

6.2 Insights into the nanostructure-electrical property relationship in Sepia eumelanin

Considering the results presented in chapter 5, the paracrystalline structure reported by Cheng J. et al. [111, 112], and the hierarchical model of Sepia eumelanin can serve as the basis to provide insights into the nanoscale electrical response. Paracrystallinity is defined as an intermediate state between crystalline and amorphous structures. In materials science, a paracrystalline structure is a

type of ordered structure that is similar to a crystalline structure, but with some degree of disorder or irregularity. The structure is characterized by patterns and arrangements of atoms or molecules that are not perfectly aligned, resulting in a range of different spacings between the atoms or molecules. This creates a pattern that is not periodic but has some degree of order and periodicity that is characteristic of crystalline structures. In other words, there are fluctuations in atomic position coordinates leading to a lack of long-range order [208, 209].

Paracrystalline structures can be found in a wide range of materials, including metals, ceramics, polymers, and even biological materials like proteins. They are often studied using techniques like X-ray diffraction or transmission electron microscopy, which can reveal the underlying atomic or molecular arrangement and help to understand the physical properties of the material. Due to several possibilities of intra- and intermolecular interactions, [210] one can have in some materials paracrystalline superstructures⁶ formed by supramolecular aggregate units [211-213].

In eumelanin, paracrystalline domains are associated with protomolecules (1-2 nm) in which the molecular ordering is in the π - π stacking direction. They are closely packed through the above-mentioned physical interactions, building up supramolecular units in more-or-less high order. As natural eumelanin is extremely heterogenous, its structure is also characterized by the molecular packing disorder leading to short-range order (i.e., few angstroms) with aggregations occurring through the nanoscale stacks and there is no long-range order [214]. In Figure 5.5, we proposed a relationship between the nanostructures and the electrical conduction of the eumelanin biopigment.

Briefly, one can consider that the internal structure of sepia granules is neither well-ordered nor amorphous as is mostly the case in organic semiconductors where the charge carrier mobility is highly impacted by the sample processing routes (vacuum deposition, solution processing, recrystallization, annealing, etc.). In fact, high-performance organic semiconductors do not require long-range order to yield high mobility. Noriega et al. have also demonstrated that charge carrier transport in small molecule organic semiconductors mainly relies on interconnected aggregates that promote more efficient intra and intermolecular charge motion [215].

⁶ A superstructure is a structure also known in biological systems, which consists of substructures that are either equal or very similar in configuration. The arrangement of these substructures within the superstructure is referred to as a framework.

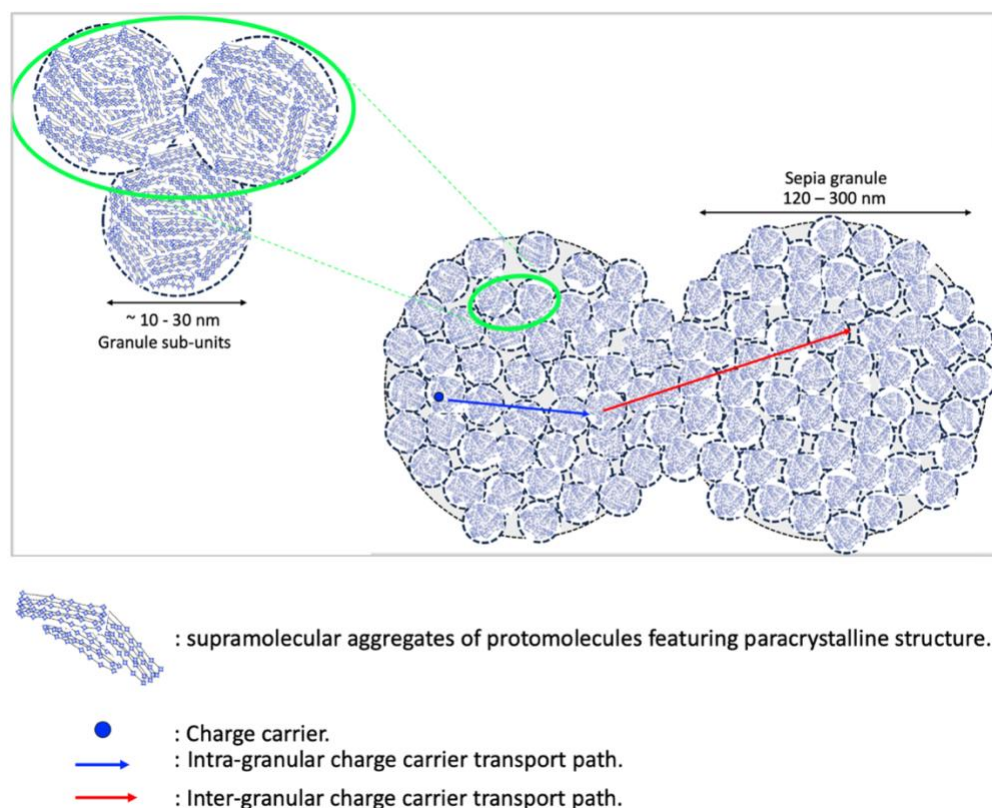


Figure 6.1. A schematic model of a fundamental relationship between the nanoscale structure and macroscopic charge carrier transport in sepia eumelanin.

The intra-granular electrical conduction of sepia eumelanin can be tentatively associated with protomolecule aggregates which are likely the constituents of particle-like subunits of each granule. In particular, the short π - π stacking distance (~ 3.4 Å) is expected to facilitate the intermolecular charge transfer between molecular segments [216, 217]. Inter-granular charge carrier transport occurs by taking advantage of structural overlap at the contact between granules that are clearly shown in HR-AFM images (Figure 5.2 (a) et (b)).

Finally, the existence of medium order at different length scales through paracrystalline state paves the way for exploiting the (macroscopic) electrical and optical properties of eumelanin. A device configuration with a nanoscale interelectrode distance that allows quantifying the charge transport mobility is still required to establish the transport physics model for (bio-sourced) eumelanin and therefore shed light on its semiconducting behaviour.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Organic semiconductors are emerging as a promising class of materials for electronics because of their interesting properties such as tunability of the molecular structure by chemical synthesis, mechanical flexibility, and lightness. One of the challenges in developing high-performance organic electronic devices is the high contact resistance at the metal-semiconductor interface and low carrier mobility due to their inherent structural disorder. Research at the nanoscale is of utmost importance for understanding structure-property relationships in this class of materials, a key step leading to technological applications.

This Ph.D. thesis is devoted to the bio-pigment eumelanin that features interesting properties, such as humidity-dependent electrical response and, in principle, biodegradability making it an interesting material for sustainable (green) organic electronics. It focuses on the band structure, nanoscale structure, and magnetic properties of eumelanin.

Initially, we worked to locate the HOMO (analogue to valence band edge) and LUMO (analogue to conduction band edge) energy levels using model systems of eumelanin, in film form. DHI- and DHICA-based films were prepared by solution processing (i.e., DHI, DHICA, AISSP-DHI, AISSP-DHICA) and thermal evaporation (i.e., Evap-DHI, Evap-DHICA) for UPS and IPES characterization. Differently processed films led to differences in the band structure.

The values of the HOMO levels (for all samples), as obtained from the measured ionization energies (E_I), were in the range of 5.34 - 5.80 eV. The E_I values are lower for AISSP-DHI and AISSP-DHICA samples than in their DHI and DHICA counterparts (see Table 4.1). This indicates that the AISSP processing route impacts the electronic structure of eumelanin, with HOMO levels at lower ionization energies. This can be explained by considering the polymerization of DHI and DHICA [186], shifting the HOMO energy levels at lower energies. Electron affinities (χ_E) were measurable for 3 samples (i.e., prepared in glove box, vacuum) namely DHI ($\chi_E = 3.80$ eV), Evap-DHI ($\chi_E = 4.0$ eV), and Evap-DHICA ($\chi_E = 3.9$ eV) (see also Table 4.1). On the other hand, DHICA, AISSP-DHI, and AISSP-DHICA did not feature reliable χ_E values.

There are various reasons including the structural disorder of the surface of the films which is not suitable for the IPES technique. This disorder could be induced by the polymerization at ambient atmosphere which was not sufficiently controlled during the AISSP protocol.

We further worked to elucidate the relationship between the nanoscale structure of Sepia eumelanin and its electrical response using atomic force microscopy (AFM) and its conductive AFM derivative. HR-AFM images showed quasi-spherical granules with diameters in the range between 120 and 300 nm. Each surface of granules is characterized by protrusions with a width average equal to 18.5 ± 6.4 nm and a height average equal to 3.0 ± 1.6 nm. Our results are consistent with the literature and thus support the hierarchical development model of sepia eumelanin. Considering the size of protrusions, they are comparable to about 2-10 packed protomolecules, which are fundamental nano-aggregate units in the molecular and supramolecular buildup of sepia eumelanin, consisting of mixed stacked planar and twisted oligomeric structures.

The C-AFM scanned on sepia-PVB printed films revealed a nanoscale electrical response of sepia, resulting in the establishment of conductive paths from the gold substrate through Sepia granules to the c-AFM tip. The observed C-AFM current is explained based on the paracrystalline structure, associated with granule subunits leading to a medium-range order which characterizes the supramolecular buildup of sepia eumelanin, allowing charge carrier transport at different length scales (from one to several granules). However, AFM does not reveal the internal structure of Sepia granules. Another experimental technique that allows one to probe the internal structure of granules such as small-angle neutron scattering (SANS) or wide-angle X-ray scattering (WAXS) would be useful to support our results.

The results related to the band structure and nanoscale studies pave the way toward defining suitable eumelanin-metal electrode interfaces for efficient charge carrier injection and charge transport, owing to similarities between the supramolecular structure of DHI/DHICA synthetic films and that of Sepia at the protrusions length scale. We are aware that this is a simplified point of view because there is no possibility to give a direct correlation between the structure from chemically controlled building blocks and the one of Sepia which naturally builds up in uncontrolled and unknown pathways.

In the hypothesis that the functional properties of eumelanin will bring to devices with acceptable technical performance, there will be a need for a scaled-up production. There are currently several

sources of eumelanin with various production alternatives such as biotechnology routes (e.g., microbial production from biomass [218-221]), which are promising to yield enhanced eumelanin production for (bio)electronic applications.

The findings of this PhD thesis pave the way for defining the structure-property relationship towards the development of sustainable organic electronic devices using (bio-sourced) eumelanin as an active material. Our study on the magnetic properties (presented in Appendix A) also opens the window to exploring eumelanin pigment in organic spintronics, an emerging research field that has defined new device concepts like spin-OLEDs and magnetic field sensors [222, 223].

7.2 Recommendations

- 1) To study charge carrier injection mechanisms, one should carry out the electrical measurements by selecting metal electrodes that minimize the injection of holes for all the samples studied whose HOMO levels were in the range 5.34 -5.56 eV (relative to vacuum level). Metals like Pt (110): 5.53 eV, Pd (100): 5.48 eV and Au (111): 5.33 eV could be used. For films (Evap-DHI, Evap-DHICA, DHI) for which LUMO was in the 3.8 - 4.0 eV range (relative to vacuum levels), one will also need to consider metal electrodes suitable for injecting electrons like Ag (100): 4.10 eV and Al (110): 4.23 eV. However, Ag or Al electrodes should be kept in a suitable atmosphere and run the electrical measurements in a vacuum to protect them from oxidation.
- 2) Due to the insolubility of natural sepia eumelanin, we recommend patterning a nanometric interelectrode distance for both natural and synthetic forms. A device configuration with a 200-300 nm channel prepared by electron beam lithography is feasible to establish the physics that applies to the intragranular charge carrier transport in (bio-sourced) eumelanin. It seems to us interesting to repeat the same experiments on DHI- and DHICA-films spin-coated on pre-patterned silicon dioxide (i.e., 100-300 nm of channel) substrates to bridge the film growth from the controlled molecular structure in synthetic molecules with the electrical response of the natural system.
- 3) Another study that interested this PhD thesis was to explore the magnetic properties of sepia eumelanin biopigment. To further understand the origin of its electrical response, we proceeded to study its magnetic behaviour as a function of humidity. To do so, electron

paramagnetic spectroscopy (EPR) and vibrating sample magnetometer (VSM) measurements were conducted at Polytechnique Montreal. A chapter on this study is presented in Appendix A with preliminary results that paved the way for further experimental research proposed at the end of the Appendix A.

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APPENDIX A. HUMIDITY-DEPENDENT MAGNETIC PROPERTIES OF SEPIA EUMELANIN

A.1 Magnetic phenomena

Particles with nonzero spin $\vec{S}$ such as electrons, protons, and neutrons are characterized by magnetic moment $\vec{\mu}$ proportional to the spin as

$$\vec{\mu} = \gamma \vec{S} \quad (\text{A. 1.1})$$

where $\gamma = g \frac{e}{2m}$ is the gyromagnetic ratio and g is the g-factor which depends on the particle. Certain materials exhibit magnetic properties due to the magnetic dipole moment of their atomic constituents. The magnetic dipole moment of an atom mainly arises from three contributions: (i) the orbital motion of electrons around the nucleus contributes to the orbital magnetic moment, (ii) the spin angular momentum of the electrons that leads to the magnetic moment, and (iii) the contribution of nuclear spin which is typically neglected as it is 1000 times weaker than the electron spin.

The applications that explore the use of magnetic materials are typically based on inorganic compounds often metals or ceramics. Most magnetic phenomena arise from unpaired electron spins typically in transition metal- or lanthanide-based compounds [224]. However, magnetic organic materials have recently emerged, specifically, those with unpaired electron spins in molecular orbitals which can interact with each [225, 226].

The interactions of spins determine the magnetic behaviour of the material, whether it is a metal, ceramics, or organics [227]. The magnetization (M) of a material is generally observed by its response to being attracted or repelled by an external magnetic field (H_0) applied to it. It is quantified by magnetic susceptibility χ (i.e., the magnetization by the magnetic field: M/H_0), which is meaningful when it is constant with H_0 . There are five basic categories of magnetic behaviour which are:

Diamagnetism. All materials exhibit a slight repulsion to applied magnetic fields due to the electrons filling the atomic orbitals. This phenomenon is called “diamagnetism” identified with a negative susceptibility ($\chi < 0$). However, the phenomenon is particularly weak and will therefore be dominated by other magnetic effects, in a material having a coordinated alignment of its magnetic moments.

Paramagnetism. Magnetic behaviours, aside from diamagnetism, are observed in materials that have unpaired electrons in their atomic structures. Paramagnetic materials are characterized by

atomic magnetic moments that are not coupled and randomly oriented without long-range order (See Figure A.1.1 (a)). Under the applied magnetic field, the magnetic moments will align in the direction of the field. Their magnetization immediately disappears in the absence of the field H_0 . The susceptibility can be due to delocalized electrons, it is the Pauli paramagnetism, in which spin-up and spin-down electrons in the conduction band are equal. An external magnetic field breaks the degeneracy between the spin-up and spin-down bands, thereby affecting a small fraction of electrons that align with the external field. This results in a positive susceptibility, which is temperature-independent and depends on the density of states at the Fermi level [228]. On the other hand, susceptibility could vary with temperature in some materials where thermal fluctuations can be strong with respect to interactions between atomic magnetic moments. This is referred to as Curie-Weiss paramagnetism described by the relation [229] :

$$\chi = \frac{C}{T - C_\theta} \quad (\text{A. 1.2})$$

Where C is the Curie constant (emu.K.mol^{-1}) and C_θ is the Curie-Weiss temperature (K).

Ferromagnetism. Atoms with non-zero magnetic moments, when densely packed in crystals, can lead to ferromagnetic order. These magnetic moments, upon being close, strongly interact to align parallel into crystal domains as illustrated in Figure A.1.1 (b). There is spontaneous magnetization even without an external magnetic field. When a magnetic field is applied to ferromagnetic domains, their magnetic moments start to rotate until they are aligned in the direction of the field. The susceptibility becomes large at lower temperatures and diverges at the phase transition temperature (i.e., Curie temperature) above which the material becomes paramagnetic [230]. The magnetization is the function of the applied magnetic field following the Langevin relation:

$$M(H_0) = M_S \coth\left(\frac{\mu H_0}{k_B T}\right) - \coth\left(\frac{\mu H_0}{k_B T}\right) \quad (\text{A. 1.3})$$

where M_S is the magnetization at saturation, which corresponds to a state where all spins become aligned in the direction of the external magnetic field H_0 . As H_0 increases, M increases until a certain value H_s , called the saturation field corresponds to the saturation magnetization. Further increase of H_0 will not increase M . The $M(H_0)$ curves usually do manifest a hysteresis loop from which one can deduce the residual magnetization M_r remaining when the field H_0 is cut off as well as the strength of reverse magnetic field (H_c) that could completely demagnetize the material.

When the external magnetic field is applied to a magnetic material is removed, the magnetic material will not lose its magnetic property immediately. There exists some residual intensity of magnetization in the specimen even when the magnetic field is cut off. This is called residual magnetism (or) retentivity.

Antiferromagnetism. Figure A.1.1 (c) shows the spin order of antiferromagnetic materials. The interacting adjacent dipole moments are antiparallel with the same magnitude. The behaviour is characterized by a positive susceptibility. As temperature increases the susceptibility also increases and reaches a maximum value at a temperature called Néel temperature T_N . Above this point, the magnetic order becomes paramagnet and susceptibility starts decreasing [230].

Ferrimagnetism. This magnetic order refers to a spin configuration where multiple domains (or sublattices), consisting of distinct spins, coexist. Within a sublattice, the spins align uniformly but are in opposition to the spins of another sublattice (Figure A.1.1 (d)). This arrangement leads to spontaneous magnetization as well [231].

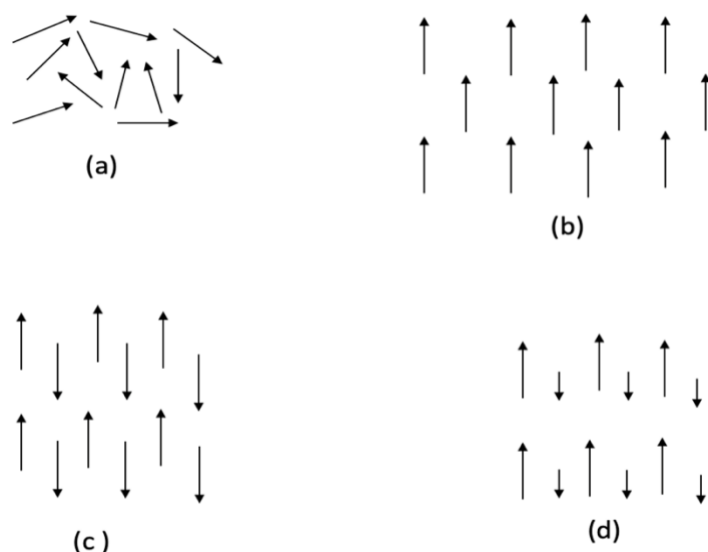


Figure A.1.1 Basic magnetic orders in materials: (a) paramagnetic behaviour (with disordered spin orientations), (b) ferromagnetic ordering, (c) antiferromagnetic ordering, and (d) ferrimagnetic ordering.

A.2 A study on the magnetization of sepia eumelanin

Magnetic behavior of eumelanin. Literature reports a paramagnetic behaviour of eumelanin in both solid-state and solution, indicating the presence of unpaired spin radicals [232-235]. There exist several chemical and physical processes that have been shown to induce distinct changes in

the concentration of radicals in eumelanin. The electron paramagnetic resonance (EPR) studies revealed that the free radicals are partially or completely quenched by lowering the pH in the eumelanin solution [236]. On the other hand, eumelanin treatments with reducing agents enhance the free radical content in non-aqueous media in the presence of metals, whereas it is decreased when the treatment is conducted in an aqueous media [237]. The eumelanin radical species possess structural and electronic requirements for chelation leading to interactions with metal ions (i.e., metal binding sites in DHI and DHICA) that impact the EPR signal, namely the g -values and line width, of both synthetic and natural eumelanin. Such spectral changes are associated with intrinsic and extrinsically induced radicals [238]. Studies by A. B. Mostert *et al.* showed the paramagnetic behaviour of eumelanin is water-driven through the comproportionation equilibrium reaction (see scheme in Figure 2.4) that regulates the relative concentrations of HQ, QI, and SQ redox forms of the eumelanin building blocks [19, 239, 240].

Two types of free radicals are known in eumelanin: intrinsic carbon-centered radicals (CCR) that result from the polymerization process, and extrinsic radicals associated with the semiquinone radicals (SQ). SQ are considered mobile charge carriers and can be observed in highly hydrated eumelanin (see also section 2.2.2), while the CCR do not appear to have any role in the electrical properties of eumelanin [19, 239, 240]. Free radicals in eumelanin can also be activated by light where excited triplet states are involved [241, 242]. In general, this happens when an electron is excited to a higher energy level, leading to the formation of either a singlet or a triplet state. In a singlet state, the electron maintains the same spin orientation as in its ground state, while in a triplet state, the excited electron maintains a spin orientation that is parallel to that of the other unpaired electron (see Figure A.1.2).

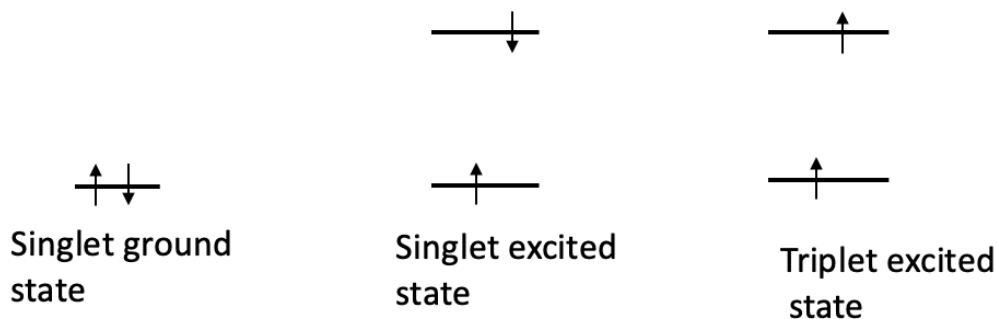


Figure A.1.2 Electron spins in the ground and excited states.

Considering that the concentration of semiquinone groups is affected by both light and water [240], the electrical conduction mechanisms involving these two parameters remain unclear.

Briefly, the mechanisms related to the magnetic properties of eumelanin remains are complex and less understood. Moreover, the mechanisms involving humidity in mixed ionic-electronic conduction still require more insights to be classified. This prompted us to study the impact of humidity on the magnetic properties of sepia eumelanin which is highly conductive to shed light on the origin of its electrical response at the molecular level, which we associated with the packing of nanoaggregate units within granules (see results in Chapter 5).

A.2.1 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) also known as electron spin resonance is a spectroscopic technique for studying materials with unpaired electrons, quite useful in the understanding of transition metal compounds, organic/inorganic free radicals, and biomacromolecules.

It is a versatile and non-destructive method that explores the excitation of electron spins by microwave radiation. Basically, the spin of unpaired electrons in a molecule or compound can align in two different spin states ($m_s = \pm 1/2$) when placed in a strong magnetic field H_0 (i.e., $E = -\vec{\mu} \cdot \vec{H}_0$). The alignment is either along the direction of the magnetic field (parallel, $m_s = -1/2$) or opposite (antiparallel, $m_s = +1/2$) to the direction of the applied magnetic field. This results in two energy states which are $E_{-1/2} = E_{\downarrow} = g\mu_B H_0/2$ (higher energy level) and $E_{1/2} = E_{\uparrow} =$

$-g\mu_B H_0/2$ (lower energy level), where g and μ_B are respectively the proportionality factor (or g -factor) and the Bohr magneton.

Therefore, when electromagnetic radiation (typically a microwave) with a frequency ν is incident to the sample, there could be electronic transitions from $E_\uparrow$ to $E_\downarrow$ corresponding to energy difference.

$$\Delta E = h\nu = E_\downarrow - E_\uparrow = g\mu_B H_0 \quad (\text{A.1.4})$$

Figure A.1.1 illustrates the energy band diagram established in the presence of the magnetic field.

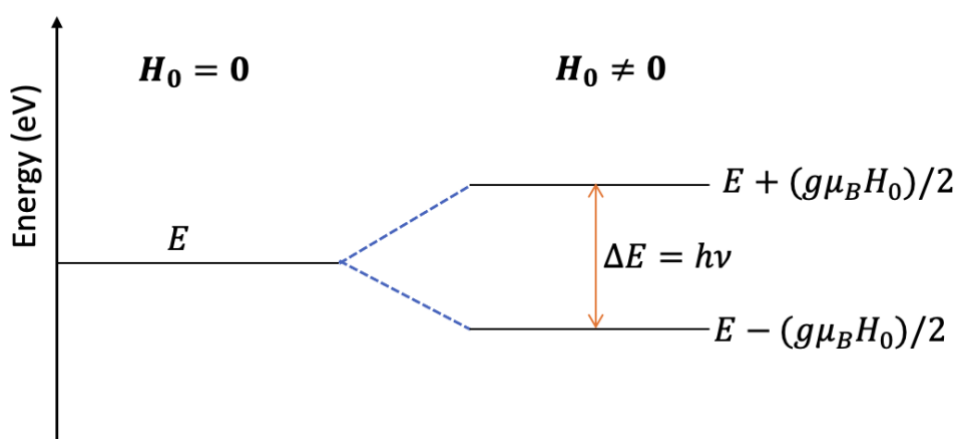


Figure A.2.1 Energy band diagram of two electronic states created by an external magnetic field. The energy difference ΔE increases linearly with increasing the strength of the magnetic field.

An EPR (Electron Paramagnetic Resonance) spectrum is produced by holding the radiation frequency fixed and changing the magnetic field. The absorption occurs when the magnetic field adjusts the energy gap (ΔE) between the two spin states equals the energy of the constant radiation. This matching point of the magnetic field is called the resonance condition. Since spectra can be produced using different frequencies, the resonance field is not enough to uniquely identify substances. Nevertheless, the g -factor that relates the energy difference to the magnetic field and frequency can provide more useful information for identification. For a free electron, the proportionality constant is equal to 2.00232. In the case of organic radicals, this factor is generally close to the free electron's value, with a range between 1.99 and 2.01. On the other hand, for compounds containing transition metals, there is a broad variation in this value, from 1.4 to 3.0, owing to the effects of spin-orbit interaction and zero-field splitting. Our approach was to

determine the nature of electron spins from the g factor and study their behavior under different humidity conditions, which play a role in the electrical properties of eumelanin.

A.2.1.1 Experimental configuration for the electron paramagnetic spectroscopy

The EPR spectrometer used in this thesis is located at Polytechnique Montreal in the laboratory of Professor David Ménard, who, with Dr Christian Lacroix (research professional), contributed to carrying out the measurements and interpreting the results.

In our experiments, our samples were sepia eumelanin powders obtained from extraction, which were distinguished in dry and hydrated states prior to the measurements. To hydrate the powder, a Pyrex glass containing a potassium salt solution (K_2SO_4 : 100 mg/ 50 ml) was inserted into the moisture chamber, which was ventilated with a fan to uniformly moisturize the environment. The relative humidity in the chamber was sensed using the USB portable hygrometer (Omega Engineering Inc., Model OM-EL-PLUS) that could detect the high relative humidity level in the range between 75%-85%RH. Afterwards, one powder sample was kept in the chamber for 48 hours while another powder was stored in the glove box for one week. The former was named “wet powder” and the latter “dry powder”.

A small conical glass container allowing the analysis of approximately 68 - 75 mg was used. The glass container with the powder was glued to a quartz rod using double-sided tape. The rod (sample holder) was a cylindrical rod of 1 mm in diameter made of quartz to minimize microwave losses.

Typically, the sample is placed inside a metal resonant cavity, located in the middle of an electromagnet coupled with the coils, the power source, and the control box. The electromagnet allowed the generation of a magnetic field between 0 and 2 T (20 kOe), which could be adjusted by a control box using buttons or using a voltage between 0 and 10 V. A gaussmeter (Model 475 form Lashore) was used to measure the magnetic field using a Hall effect probe.

During the EPR measurements, a static magnetic field H_0 and a high-frequency magnetic field H_{ac} (GHz), perpendicular to H_0 , are applied to the sample (Figure A.2.2), where the frequency of the field H_{ac} is fixed while the strength of the field H_0 is varied. In this configuration, the H_{ac} field promotes the precession of the magnetization around the effective field H_{eff} (which is generally parallel to H_0) when the resonance condition is reached.

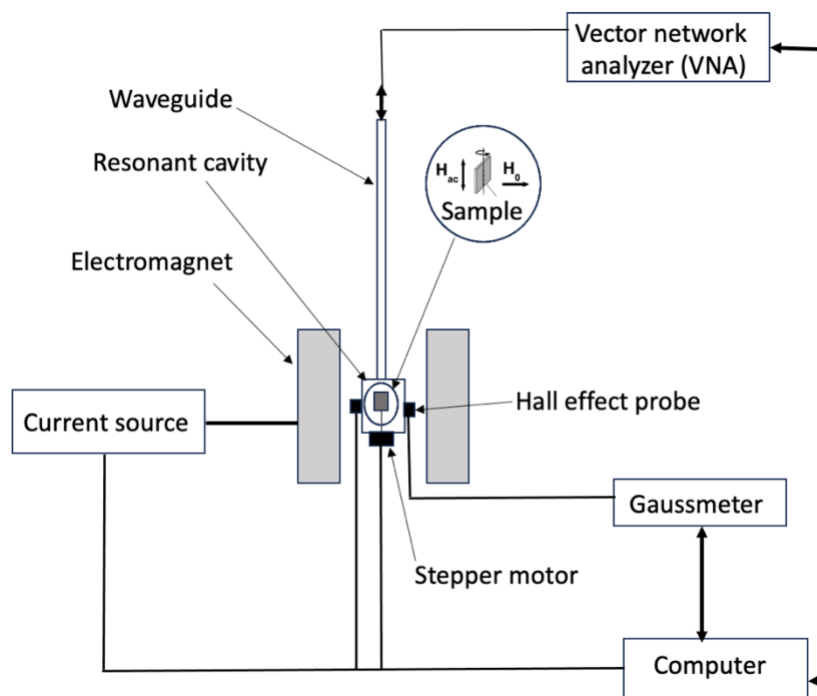


Figure A.2.1 A representative scheme of the EPR spectrometer, adapted from [243].

Finally, the EPR signal was generated and detected through the vector network analyzer (VNA, Model 2 ports PNA-L 5230A 10 MHz - 40 GHz from Agilent company). The measurement system was controlled by a computer using software programmed by Christian Lacroix in Lab-VIEW. The software communicates with the network analyzer and gaussmeter using the IEEE-488 (GPIB) standard. It also controls the strength of the continuous magnetic field. Thus, the data are collected by the computer for analysis. From the spectrum intensity (absorption accounts vs magnetic field), the EPR peaks are identified at the resonant fields which allow us to calculate the corresponding g-factors.

A.2.2 Magnetometry

A.2.2.1 Working principle

The magnetometry technique consists of using a vibrating sample magnetometer (VSM) to measure the magnetic moment (i.e., the magnetization per unit of volume) of a sample material placed in an external static magnetic field. The system converts the dipole field of the sample into an AC electrical signal. The working principle relies on the fact that a magnetic sample sinusoidally

vibrating under an applied external magnetic field generates a varying magnetic flux. The induced voltage is proportional to the sample's magnetic moment if it is assumed as a dipole [244].

In the VSM setup (figure A.2.3), invented by Simon Forner in 1955 [245]), the sample to be analyzed was glued at the base of a Pyrex rod tube (i.e., sample holder) using double-face paper tape. The rod tubes fabricated by Pyrex allow measurements in the temperature range of 130-900K with a low diamagnetic contribution. Then, the end of the sample holder is inserted in the head of the vibrator which is made of linear actuators or modified audio speakers such that the sample is centred in the field of an external electromagnet. A static magnetic field H_0 produced by the electromagnet is measured by the Gaussmeter.

As the sample is vibrating, an AC voltage is induced within detection coils. The induced voltage is measured through the lock-in amplifier using the piezoelectric signal as its reference signal. The lock-in principle of measurement compares the voltage induced in detection coils with the signal used for the vibration of the rod which allows to remove of the parasitic signal (noise) and amplifies the sample signal. The VSM operation is controlled by a computer with the LABVIEW software, for instance, that communicates with the IEEE-488 norm (GPIB).

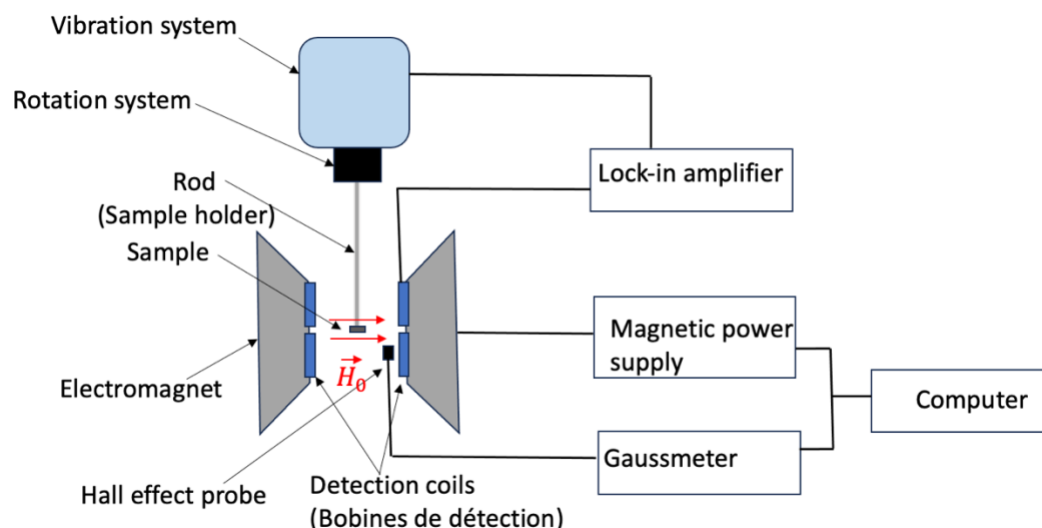


Figure A.2.3 A scheme of the experimental configuration of a VSM, adapted from [243].

A.2.1.2 Measurements of the magnetization

In this thesis, an EV9 VSM model from ADE Technologies was used to measure the magnetization of sepia eumelanin pellets as a function of the strength of the magnetic field and the temperature.

The pellets were prepared by Josianne Lefebvre, a research professional in the Department of Engineering Physics at Polytechnique Montreal. To this end, the sepia powders were loaded at 6.5 metric tons using bench-top manual presses (CARVER Inc.), allowing us to achieve thicknesses between 1 - 5 mm depending on the amount of the loaded powder. They were afterwards diced in an approximately rectangular shape (nominal size about 4 - 5 mm in width and 8 - 9 mm in length) with a clean stain steel blade.

The procedure to measure the sample requires several steps. If the sample to be analyzed is magnetic film deposited on a diamagnetic substrate, the resulting signal will be a contribution of the film, the substrate, and the rod. One has therefore to measure the bare substrate to subtract its contribution from the sample signal. It implies knowing the mass of the sample and the substrate. This information will allow us to measure the magnetic moment of the film by subtracting the substrate contribution.

A calibration sample (Nickel disc) was used to set the rod position and calibrate the measurement scale of the magnetic moment. Afterwards, the magnetic moments are measured as a function of parameters such as temperature, and the strength of the magnetic field. Finally, the sample holder (Pyrex tube) is also measured as a function of the same parameters. This last measurement is needed for data analysis to remove the tube contribution. Measurements of the magnetization at different temperatures (130-380K) were carried out by using an oven tube connected to a thermocouple. The pellet glued on the rod was inserted into the tube while connected to the vibration system. For high-temperature measurements, a heat N_2 gas was pumped in the oven, thus allowing the measurements at ambient conditions. Low-temperature measurements were done by cooling the N_2 gas by the liquid N_2 .

A.2.3 Results

We investigated the behaviour of the electronic spins of hydrated and dry extracted sepia powders from EPR experiments, a method that has already provided insights into the free radical species in eumelanin [246, 247].

With a radiation frequency $\nu = 9.486 \times 10^9$ Hz, we observed an EPR signal at a resonant field $H_0 = 3365$ Oe = 0.3365 T (Figure A.2.4). By using equation (A.1.1), the corresponding g-factor is $g \approx 2.0141$, which is in the range of values attributed to organic radicals (typically ranging from 1.99 to 2.01), close to that of free electrons. We cannot tell what the radical is exactly associated

with the observed peak. Most importantly, one should be aware that the g -factor is sensitive to the electronic structure of the radical, the nature and number of heteroatoms [248]. The paramagnetic behaviour has been ascribed to carbon-centred radicals in the eumelanin [235, 249]. The EPR peak is more intense in dry powder (see Figure A.2.4 (a)) than the hydrated powder (Figure A.2.4 (b)) that was exposed to a high-humidity atmosphere (76 %RH). This is supported by the literature, i.e., the density of electron spins decreases with humidity.

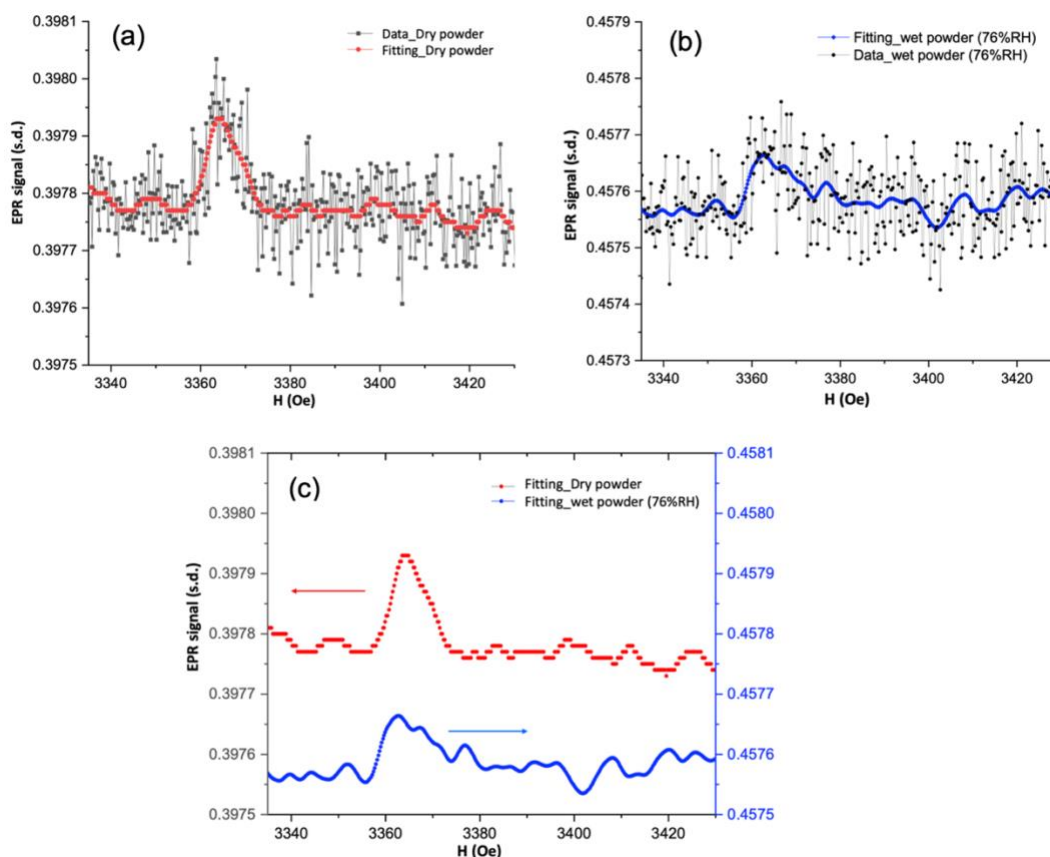


Figure A.2.4 EPR signal peaks (a) dry and (b) wet pellets of extracted sepia eumelanin. Fitting is indicated in (c) showing a clear decrease of paramagnetic behaviour in hydrated (wet) sepia eumelanin.

To elucidate the type of magnetism and the relationship between electrical conductivity and magnetic order, we measured the magnetization of the sepia pellets from the VSM. The total of the magnetization of the pellet (emu/g or $\text{kA.m}^2/\text{kg}$) as a function of the external magnetic field was obtained by subtracting the magnetic moment of the sample holder (i.e., rod) from the measured total magnetic moment and then dividing by the mass of the sample. Practically, the paramagnetic and diamagnetic contributions of the sample are extracted from the plots by considering a linear fit

at data corresponding to higher magnetic fields (see illustration in Figure A.2.5 (a)). Then, the ferromagnetic contribution (Figure A.2.5 (b)) is deduced by removing other contributions (i.e., diamagnetism + paramagnetism) from total magnetization.

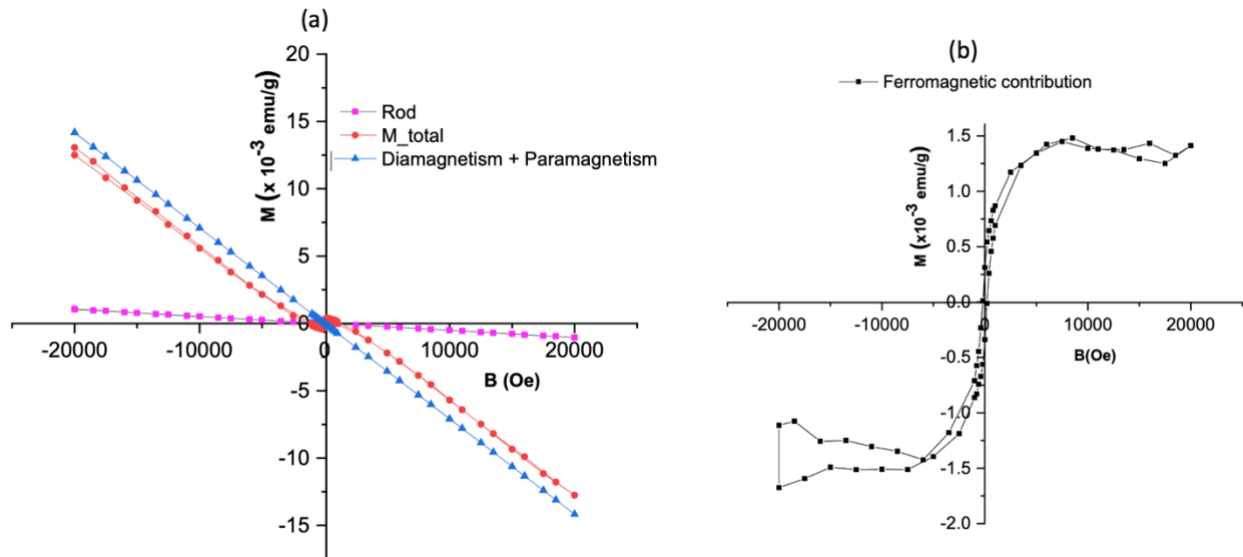


Figure A.2.5 Measurements of the magnetization as a function of the magnetic field applied on the sepia eumelanin pellet at room temperature. In (a) the total magnetization is obtained by subtracting the sample holder's (i.e., rod) contribution. The combined paramagnetic and diamagnetic contributions of the sample are obtained from the slope of the linear fitting at higher values of the magnetic field. In (b) the ferromagnetism contribution is the total magnetization after subtracting the paramagnetic and diamagnetic values.

Figure A.2.5 (b) indicates ferromagnetic order obeying the typical Langevin equation (A.1.3) in sepia eumelanin at room temperature. However, measurements at different temperatures show that the saturation magnetization does not depend on temperature (Figure A.2.6 (a)). A small hysteresis could be noticed at low magnetic fields (Figure A.2.6 (b)) which increases at low temperature. In the same figure, the remanent magnetization can be evaluated at 210 K, $M_{r,210K} \approx 0.125 \times 10^{-3} \text{ emu} \cdot \text{g}^{-1}$ and the coercive field is $H_{c,210K} \approx 300 \text{ Oe}$. There is a clear temperature-dependent coercivity.

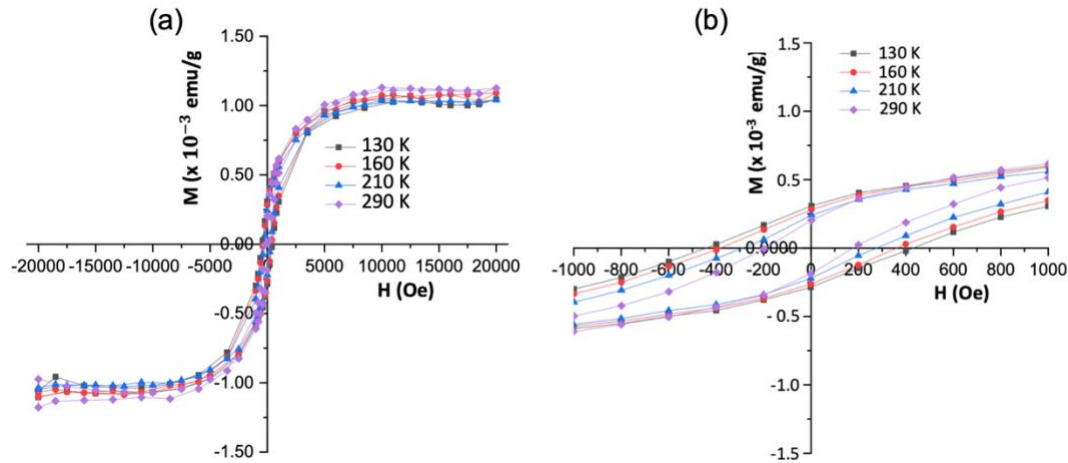


Figure A.2.6 Temperature-dependent hysteresis loop in magnetization of sepia eumelanin.

It can be noted that the measurements presented in Figure A.2.5 (b) show a saturation magnetization higher than that presented in Figure A.2.6 (a). The reason is that all these samples were stored in an ambient atmosphere where humidity was not controlled, and samples were not measured on the same day. We proceeded to run the VSM measurements with a controlled humidity on the samples as same as the EPR measurements. We specify that the calculation of the error associated with the measurements of saturation magnetization was made by considering the standard deviation $\bar{\sigma}$ given by

$$\bar{\sigma} = \sqrt{\frac{\sum (M_{Si} - \bar{M}_S)^2}{n}} \quad (\text{A.1.5})$$

where M_{Si} is the saturation magnetization of one sample at room temperature and $\bar{M}_S$ is the mean magnetization of n samples. Five samples were always kept in a dry atmosphere ($n=5$) and three samples were in dry and humid environments ($n=3$) depending on whether we wanted to increase or decrease the level of relative humidity in the sample pellets.

As observed in the EPR signal, the ferromagnetic order is also affected by the humidity. Indeed, the saturation magnetization is $M_s = 1.56 \pm 0.07 \times 10^{-3} \text{ emu/g}$ when stored in the glove box away from ambient oxygen and moisture. However, when exposed to high humidity ($\sim 85\% \text{ RH}$) for about two days, their magnetization was diminished ($M_s = 1.19 \pm 0.05 \times 10^{-3}$) (see Figure Figure A.2.7 (a)). This means absorbed water molecules affect the interaction of magnetic

moments. In addition, redrying and rehydrating the pellets showed that the process is reversible (details in Figure A.2.7 (b, c)).

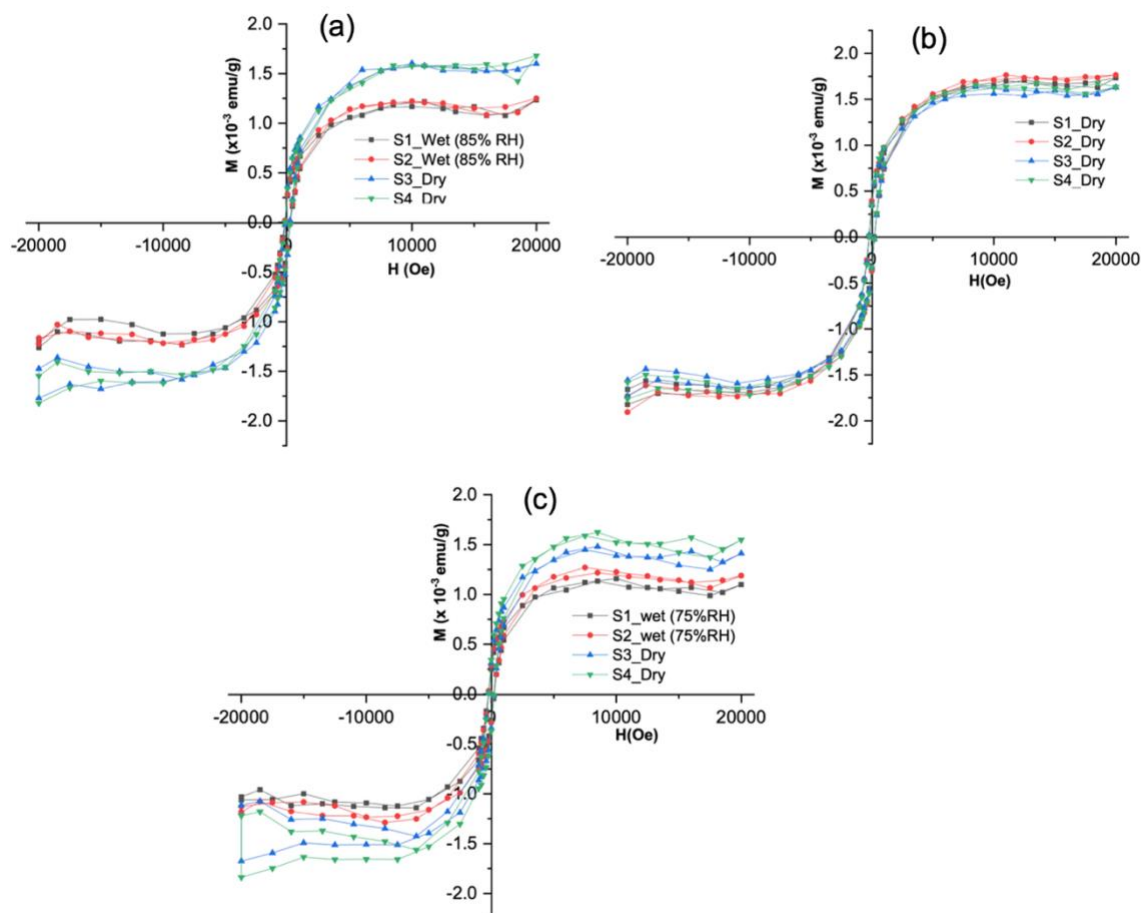


Figure A.2.7 Reversible humidity-dependent ferromagnetism of sepia eumelanin powder. S1, S2, S3 and S4 are the studied sample pellets. Samples S3 and S4 were dry as they were stored in the glovebox every time (before and after each measurement). S1 and S2 were (a) hydrated in a humidity chamber for 48 hrs, (b) dried in an N_2 glovebox ($O_2, H_2O < 5$ ppm) for 14 days, and (c) rehydrated for 48 hrs.

It is important to note that the measurements were conducted at ambient conditions. That means we ignored any change in the water content during the measurements which, fortunately, was not significant enough to hide the difference in magnetization of the two types of samples (i.e., dry, and hydrated pellets).

The measured susceptibility is negative and very small ($\chi \sim -10^{-7}$ emu.g $^{-1}$.Oe $^{-1}$). From χ -T plots in Figure A.1.8, the χ values are relatively temperature-independent. This indicates a

dominant diamagnetic behaviour. On the other hand, it is hard to observe the Pauli paramagnetism, which is due to delocalized electrons as its susceptibility response is typically weak ($\chi_{para} \rightarrow 0$ in organic compounds) because their response involves a fraction of electrons near the Fermi level [229].

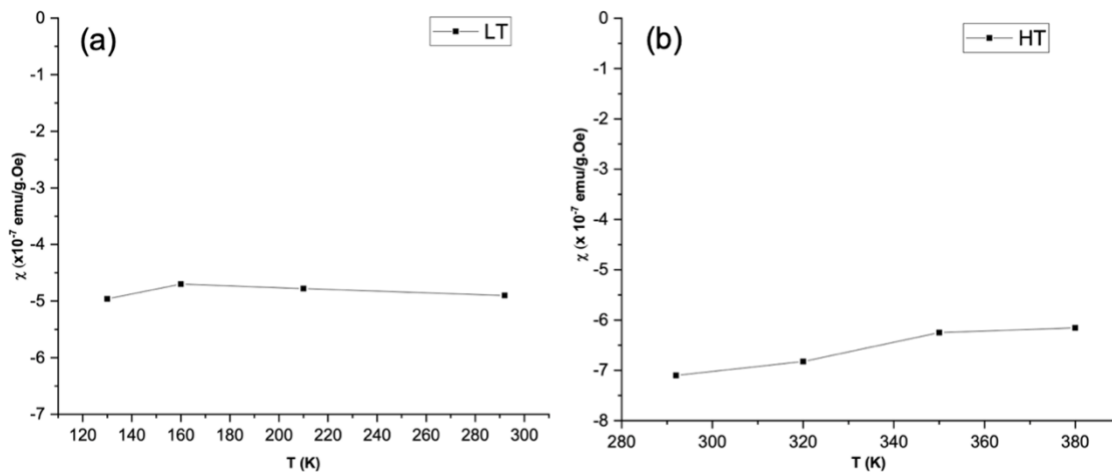


Figure A.2.8 Magnetic susceptibility of sepia eumelanin pellets measured at (a) low temperature and (b) high temperature.

We recall that sepia eumelanin powders are electrically conductive, which was also observed in Chapter 5. In the free electron model, we can assume the Landau diamagnetism in which there is an orbital movement of conduction electrons in the magnetic field. The corresponding Landau susceptibility χ_L is negative and one-third of the Pauli paramagnetism expressed as [250]

$$\chi_L = -\frac{4}{3} \frac{\gamma \delta^2}{2H_0} \quad (\text{A.1.5})$$

where γ is the Fermi surface of states per spin projection, $\delta = \hbar\omega_H/2$ is the spacing of Landau energy levels, H_0 is the magnetic field. In reciprocal space, the Fermi surface is defined as the surface that separates occupied from unoccupied electron states. However, this theoretical model of free electrons applies well to metals and rarely to organic conductors which are often characterized by a certain disorder in their structure, so the charge carriers get easily localized.

A.2.4 Discussion

Our results evidenced a negative effect of absorbed water molecules on the magnetic order of sepia eumelanin. The literature reports an increase in electrical conductivity with water content [251-254]. The role of humidity on both electrical and magnetic properties suggests a correlation between the unpaired atomic/ionic/electronic magnetic moments and the charge carriers that contribute to the conductivity. These results challenge our understanding of how charge carriers are activated by humidity. The coexistence of both paramagnetic and ferromagnetic phases at room temperature, which are decreased by the humidity of the surrounding environment reveals a complex magnetic order in sepia eumelanin.

Drying the pellet samples enhanced magnetization possibly due to π - π stacking structure and high spin states, enabling the spin exchange interactions. Spontaneous magnetization might arise from local magnetic moments (i.e., unpaired localized electrons) [255] [256]. In dry samples, the charge carrier transport could be associated with the coexistence of long-range magnetic order and localized electron states, which generally characterize conducting organic materials [257].

Now comes the question of how the humidity increases the conductivity while it decreases the magnetic order. There is evidence that humidity induces charge carrier density in sepia eumelanin, as reported in the literature [249, 258, 259]. The presence of water molecules is also expected to alter the comproportionation equilibrium reaction, form hydrogen bonds with eumelanin molecules, and induce changes in molecular conformations, leading to more free radicals associated with charge carriers that we cannot confirm are the SQ species in our measurements. In addition, the reversible effect of humidity on the magnetization suggests the generation of metastable radical ions, involved in reducing the ferromagnetic order, which are further deactivated by redrying the samples [257]. Briefly, a metastable state refers to a specific type of excited condition within an atom, nucleus, or another system that exhibits a long lifetime compared to typical excited states. However, its duration is usually shorter than that of the most stable and lowest energy level, known as the ground state.

The magnetic polaron model, as suggested by Coey et al. [260] in dilute ferromagnetic metal oxides might provide insights into the inverse correlation between magnetization and carrier concentration in semiconductors. In this model, ferromagnetic exchange is mediated by the shallow donor electrons that form bound magnetic polarons. Specifically, an electron localized at a defect site is

confined within a hydrogenic orbital. The overlapping between this localized electron and unpaired electrons of the magnetic ions facilitates a cooperative ordering of the magnetic ions akin to a percolation process. Each localized magnetic moment constitutes an effective magnetic polaron such that a ferromagnetic behaviour takes place when these polarons reach a density sufficient for percolation. Assuming δ the concentration of donors and x the concentration of the magnetic ions, there exists a polaron percolative threshold δ_p and an ion percolation threshold x_p such that ferromagnetism occurs when the concentration of localized electrons $\delta > \delta_p$ and the concentration of magnetic sites $x < x_p$. Furthermore, a sudden change in the wave function of the magnetic polaron, induced by carrier hopping between neighbouring sites, can result in a fluctuating exchange field, which may, in turn, destabilize the spin orientation of the magnetic ion, hence reducing the magnetism [261]. From this point of view, one can reasonably understand the decrease in magnetization with an increased carrier density. Our interpretation is that charge carriers magnetically interact with ionic/atomic/molecular magnetic moments in sepia eumelanin, leading to ferromagnetic order. This is more taking place in dry pellets of sepia eumelanin. As the charge carrier concentration is increased by the moisture, this might decrease magnetization. Such a negative effect on the magnetic order could be attributed to the hopping charge carriers as described by the model of Coey et al. [260].

The paramagnetic behaviour can be understood considering the hierarchical structure of sepia eumelanin, i.e., one has a mixture of particles with different sizes. We hypothesize that granule subunits could behave as superparamagnetic particles. Superparamagnetism phenomenon can occur in small magnetic nano aggregates, which are ferromagnetic single domains [262]. Within a domain, strong mutual interactions often align atomic moments, resulting in a magnetic moment significantly larger than individual atomic moments [263-265].

When a magnetic field is applied, the collection of magnetic moments tends to align in the direction of the field and saturation is reached when they are all parallelly oriented [266]. This magnetization of a superparamagnetic material vanishes after the magnetic field is switched off.

It is very important to note that there is a critical particle size, where the superparamagnetic behaviour occurs, typically a diameter ≤ 50 nm [267] [268]. Due to their small size, thermal energy can randomly alter the direction of their magnetization [262]. The time average between two directional flips of magnetization is termed the Néel relaxation time τ_N given by

$$\tau_N = \tau_0 \exp \left(\frac{K_u V}{k_B T} \right) \quad (\text{A.1.6})$$

where K_u is the magnetocrystalline anisotropy energy and V is the volume of the single domain particle. When no external magnetic field is applied and the measurement duration exceeds the Néel relaxation time, the average magnetization of the nanoparticles appears to be zero, indicating a superparamagnetic state. In this condition, an external field can magnetize the nanoparticles to their saturation point, resulting in a magnetic susceptibility significantly higher than that of paramagnets.

From the experimental data, the signature of superparamagnetism is the fact that M follows the universal function expressed by Langevin equation (A.1.3) and the absence of the hysteresis loop. The two conditions are likely satisfied in Figure 6.1.3. (a)). However, since one has a size distribution of nanoaggregates, including large granules (120 -300 nm), there can be a mixture of single and multi-domains that overlap at some temperatures [269]. Indeed, “particles that are large enough can contain many domains, in which the initial stage of magnetization is accomplished by a motion of domain walls that are relatively unimpeded by imperfections” [269]. They are called ferromagnetic multi-domains. Mathematically, when a magnetic field H is applied to a mixture of N types of particles, their magnetization M_{mix} is expressed as

$$M_{\text{mix}}(H) = \left(\frac{\sum_i^N M_i(H) f_i}{\sum_i^N f_i} \right) \quad (\text{A.1.7})$$

where $M_i(H)$ is magnetization of the i^{th} constituent and f_i is the fraction volume of this constituent. The size range of subunit granule size (6 - 40 nm) in sepia eumelanin supports the hypothesis of ferromagnetic single domains. In addition, the superparamagnetic phenomenon is also consistent with the strongly temperature-dependent coercive force revealed in Figure A.2.6 (b). We propose a scheme in Figure A.2.9 that indicates the domain size associated with superparamagnetic nanoaggregates in sepia eumelanin.

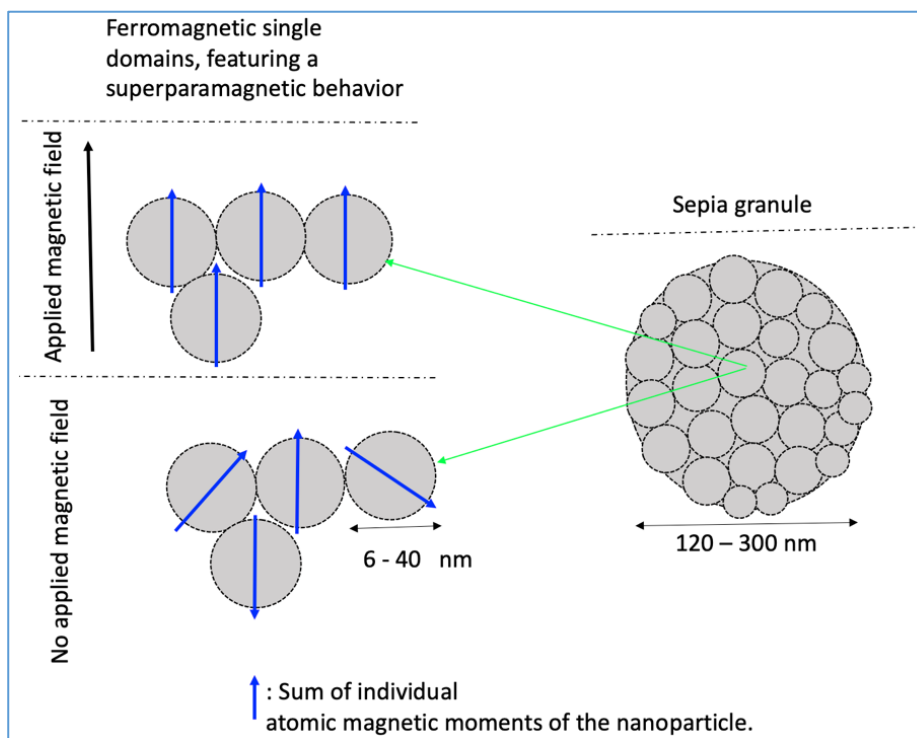


Figure A.2.9 A proposed scheme of ferromagnetic single domains in sepia granules.

A.3 Summary and perspectives

We proceeded to shed light on the origin of the observed electrical response of sepia eumelanin at the molecular level by conducting a systematic study of the magnetic properties of eumelanin at different degrees of humidity. The VSM and EPR experiments evidenced that the magnetic behaviour of sepia eumelanin is affected by humidity. Its magnetic order is complex as it involves ferromagnetism and paramagnetism. The magnetization of (dry) samples stored in a controlled atmosphere (oxygen and humidity) was higher ($M_{\text{dry}} = 1.56 \pm 0.07 \times 10^{-3} \text{ emu/g}$) compared to the one measured on (wet) samples exposed to high humidity (75% - 85% RH), which was decreased down to $M_{\text{wet}} = 1.19 \pm 0.05 \times 10^{-3} \text{ emu/g}$.

Our results hence evidenced an inverse correlation between the magnetization and the charge carriers that contribute to its electrical properties. The former is reduced by relative humidity while the latter is increased. However, it is not straightforward to figure out how the conductivity is activated by humidity in such a complex mixed protonic-electronic conducting biomacromolecule. Our observations suggest the existence of unpaired magnetic moments at the atomic or molecular level that render the bio-pigment a ferromagnetic material. The activation of the concentration of

charge carriers by humidity is paralleled with the coupling between them and the unpaired spins thereby reducing the magnetic order of the electronic spins.

Our results provide another approach to understanding the mechanisms generating charge carriers in eumelanin. We observed that the increase in SQ decreases the ferromagnetic order if we assume that the comproportionation equilibrium model is true. On the other hand, as there are several redox forms of DHI and DHICA, the magnetic properties are possibly related to free radicals not revealed such that there are spin exchange interactions easily occurring when eumelanin is more dried. Such radicals can also be carbon-centered radicals which have been suggested by Mostert et al. [247] or another redox form.

We attributed the magnetization in dry pellet samples to π - π stacking structure with an interplanar distance of about 3.4 Å that enables the spin exchange interactions between free radical ions. In dry samples, the charge carrier transport could be associated with the coexistence of ferromagnetic order and localized states, which typically characterize conducting organic materials [270].

The literature explains the increase of electrical conductivity in samples exposed to high humidity by the extrinsic water molecules incorporated in eumelanin that add protonic and electronic charge carriers [249, 258, 259]. Thus, the inverse correlation between magnetization and charge carrier concentration can be tentatively explained by the magnetic polaron model proposed by Coey et al. [260] in their study on dilute ferromagnetic metal oxides. In this model, localized charge carriers interact with unpaired spins of radical ions, leading to cooperative ferromagnetic ordering. The magnetization can be reduced due to carrier hopping that can induce a fluctuating exchange field, which may in turn alter the spin orientation of the magnetic ions. We tentatively proposed the same analogy in sepia eumelanin as the moisture activates charge carriers that interact with ionic/molecular magnetic moments, thus decreasing its magnetization.

The paramagnetic behaviour of sepia eumelanin was described by making a hypothesis that the nano aggregate subunits (6 - 40 nm) within sepia granules are ferromagnetic single domains that behave like superparamagnetic particles, characterized by a large magnetic moment. In addition, this does not exclude the existence of ferromagnetic multi-domains since there is a size distribution of nano aggregates that support the hierarchical structure of sepia, including large granules (120 - 300 nm). Such single-and multi-domains can overlap at some temperatures [269].

Hence, this study on the magnetic behaviour of eumelanin opens the door for future experimental research. We propose to use techniques such as:

- a) x-ray magnetic circular dichroism (XRMCD) spectroscopy to provide insights into the energy bands related to spin and orbital magnetic moments in the eumelanin [271] at different humidity conditions.
- b) the Fourier transform infrared (FTIR) spectroscopy for a comparative analysis of the changes in hydrogen bonding from dry to wet samples to shed light on the intermolecular interactions between water molecules and eumelanin molecular/ionic species.
- c) the neutron activation analysis to assess the elemental composition in sepia eumelanin to figure out if there are magnetic metal impurities which might contribute to the magnetic behaviour of eumelanin as its building blocks have metal binding sites.