Optical Spectroscopy for Probing the Structure-Property Relationships of Eumelanin - a Key Functional Biomacromolecule

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Theme: The Structure-Property Jigsaw Puzzle

- Establishment of the Structure-Property Relationships for Biomacromolecules (proteins, etc.)
- Focusing on the human pigmentation system - melamins

Structure:

<table>
<thead>
<tr>
<th>Primary (Å)</th>
<th>Secondary (nms)</th>
<th>Tertiary (10nms)</th>
<th>Aggregates (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QM</td>
<td>QM/Classical</td>
<td>Classical</td>
<td>Classical</td>
</tr>
</tbody>
</table>

Properties:

- Molecular:
  - relaxed geometries
  - electronic structure
  - energies
  - phonon structure

- Mesoscopics:
  - electron-phonon interactions
  - free spin dynamics
  - electron delocalisation
  - weak dispersive interactions

- Macroscopic Observables:
  - optical
  - electrical
  - photochemical
  - chemical
Where can Biophotonics & Optical Spectroscopy Help?

1. Optical probes (UV-visible-IR)
   - Electronic structure
   - Vibrational structure

2. Linking the molecular scale properties (chemical, electronic and phononic structure) to observable macroscopic properties

3. Combined imaging and spectroscopy for in vivo studies (locating pigment, confirming structure)

Our approach:
Optical spectroscopy + synthetic organic chemistry + quantum chemistry / many-body-theory + CMP + molecular biophysics

Melanin Background

- Functional bio-macromolecule found throughout nature:
  - Photoprotectant
  - Pigment
- Several types:
  - Eumelanin (predominant in humans)
  - Pheomelanin
  - Neuromelanins
  - Allo melanins
- Exotic physico-chemical properties
  - Broad band monotonic absorption in the UV & visible (black)
  - Condensed phase electrical and photoconductivity
  - Efficient non-radiative relaxation of photoexcitations
Eumelanin

- Macromolecules of indolequinones

The important questions:
- What is the correct secondary structure?
- What are the appropriate mesoscopic models linking this structure to the macroscopic properties?
- Are melanins quantum materials – how do their macroscopic properties emerge and at what length scales are quantum effects important?
- What are the broader implications for understanding structure-property relationships in other important bio-macromolecules?

- Molecular engineering of synthetic analogues with the appropriate properties as functional materials

The S-P Jigsaw Puzzle for Eumelanin

DHICA

DHI

Eumelanin

R = -H or -COOH
The S-P Jigsaw Puzzle for Eumelanin (structure)
The S-P Jigsaw Puzzle for Eumelanin (molecular properties)

$$S_3 \quad S_2 \quad S_1 \quad S_0$$

$$\pi \quad \pi^*$$

$$hf = E_F - E_0 = \text{LUMO-HOMO}$$

The S-P Jigsaw Puzzle for Eumelanin (mesoscopics)

$$E$$

$$E_C = 1.40 \text{eV}$$

$$E_F = 0.2 \text{eV}$$

$$E_V = 0.78 \text{eV}$$

$$N(E)$$

(From DC conductivity Measurements)

Overlapping $p_z$ forming $\pi$ and $\pi^*$ molecular orbitals
The S-P Jigsaw Puzzle for Eumelanin (macroscopic observables)

Solution absorption, broad & monotonic


Solid state optical gap emerging at 1.7eV

Radiative emission – weak and broad, and excitation energy dependent


Challenges:
- Broad absorption
- Low radiative yield
- Limited solubility

Solution
- Correct for probe attenuation
- Correct for re-absorption
The S-P Jigsaw Puzzle for Eumelanin (macroscopic observables - optical spectroscopy)

Quantum Yield Maps of Eumelanin

Radiative quantum yield:
- Very small
- Excitation energy dependent


Current Paradigm

Extended indole heteropolymer ➞ Delocalised $\pi$ system ➞ Amorphous Semiconductor Band structure = Broad absorption Conductivity Solid state gap

Many Body Calculations

- Relaxed geometry, energy and electronic and phonon structure calculations using NRLMOL (DFT calculations using Gaussian Orbital methods - Generalised Gradient Approximation using the Perdew-Burke-Emzerhof exchange correlation function)
- Predict the HOMO-LUMO gap for a range of monomers and small oligomers

HOMO-LUMO: 3.61eV ➞ 2.02eV
Many Body Calculations

LUMO

HOMO


Many Body Calculations - Oligomers

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Energy 1</th>
<th>Energy 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule (30)</td>
<td>3.84eV</td>
<td>3.81eV</td>
</tr>
<tr>
<td>Molecule(30)e</td>
<td>3.64eV</td>
<td>3.10eV</td>
</tr>
<tr>
<td>Dihed(Mono coupled) (26)</td>
<td>2.22eV</td>
<td>2.13eV</td>
</tr>
</tbody>
</table>

BIA 2006
Many Body Calculations - Oligomers

Broad Monotonic Absorption

Only 11 inhomogeneously broadened transitions with typical polar solvent line widths

1. Chemical disorder – macroscopic properties are the ensemble average of a number of chemically distinct species
2. Consistent with emission and excitation evidence – selective pumping of a part of the ensemble
3. “Low cost” strategy for achieving robust functionality

Summary & Conclusions

- Key objective: to establish S-P relationships, correct secondary structural model required
- Current theory (conjugated heteropolymer leading to amorphous semiconductivity) not consistent with electrical and optical data
- Subtle changes at the primary and secondary level create significant differences in electronic structure (HOMO-LUMO gap)
- Broad absorption, low radiative yield and complex excitation landscape can be explained through chemical disorder with a small number of chemically distinct species
- Chemical disorder = low cost resource?
- Optical spectroscopy key experimental tool for probing biomacromolecules

Next Steps

- Experimental confirmation of oligomer predictions
  - HOMO-LUMO gaps (absorption edge), emission and excitation spectroscopy
  - Phonon spectra (INSS) & Raman
  - Synthetic models and in vivo
- Calculations
  - Phonon spectra
  - Electron densities
  - Oscillator strengths
  - Electron-phonon coupling strength
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$$$ARC & UQ