Optical properties of stacked eumelanin protomolecules

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- Eumelanin: the most common biological melanin
- Photoprotective pigment
- Broadband **absorption** spectrum, **intensity increasing with frequency**

- Macromolecule contains 5,6-dihydroxyindole (DHI), 5,6-dihydroxyindole-2-carboxylic acid (DHICA) and their derived redox forms
  a) Detailed supramolecular arrangement of constituent protomolecules
  b) chemical structure < - - - > optical properties
  } *not fully clarified yet*

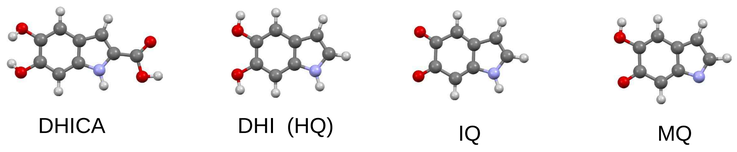
- From experimental data: stacked oligomers, 3-4 Å interlayer distance, 15-20 Å lateral size

- Kaxiras et al. → **stacked** porphyrin-like **tetramers**

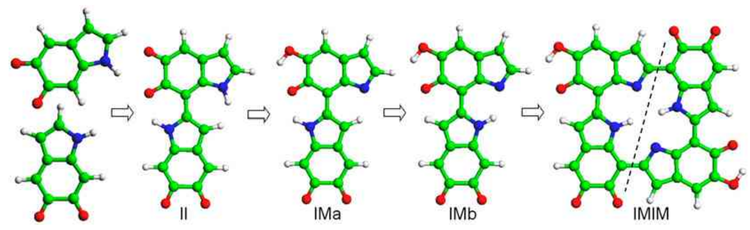
Methods
- Plane Wave DFT / TDDFT
  → "natural" way for describing (infinite) stacking; basis set convergence tests straightforward
- Codes: QuantumEspresso and Yambo

Eumelanin protomolecules:

Monomers:



Proposed **IMIM tetramer formation pathway**
S. Meng, E. Kaxiras, Biophys J. 94, 2095, (2008)

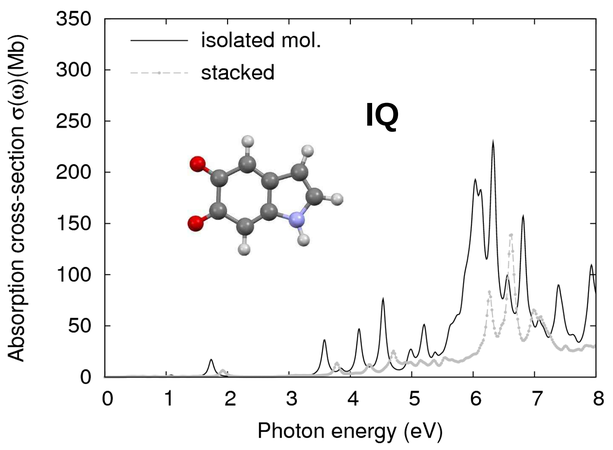


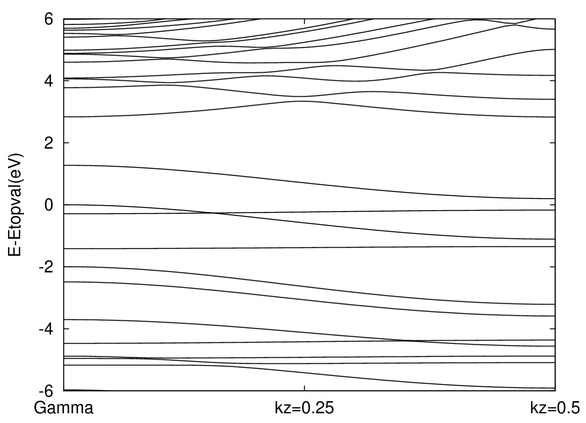
"IMIM" = 2 IQ + 2 MQ

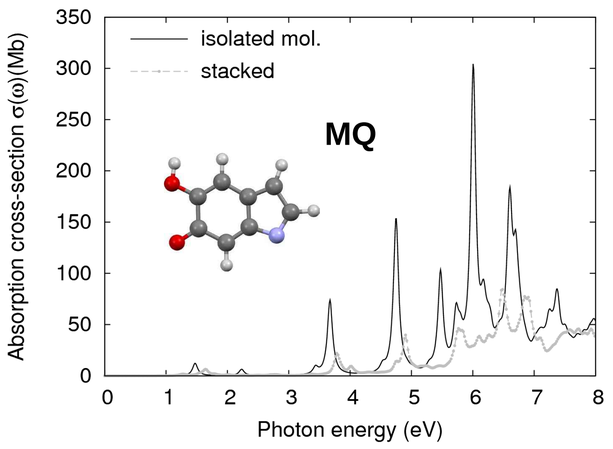
***Stacked porphyrin-like* tetramers** → explain:
- finite lateral size
- metal-binding ability of eumelanin

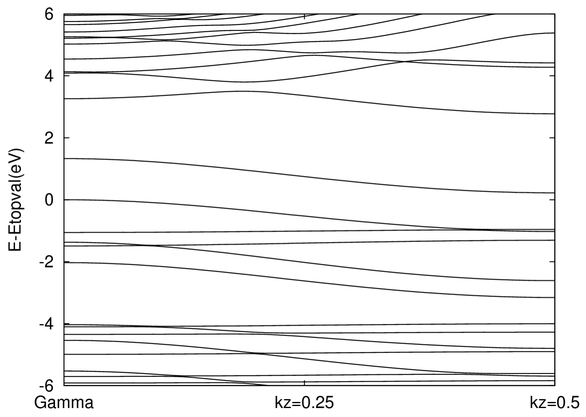
Monomers: Effect of stacking

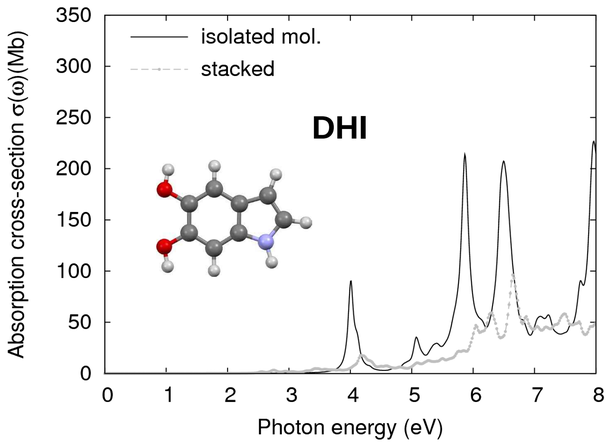
Stacked cases: band structures

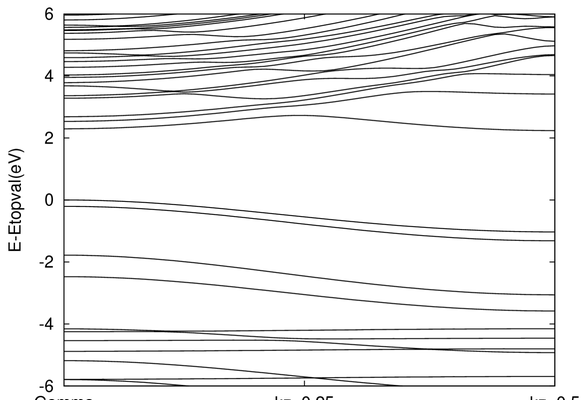




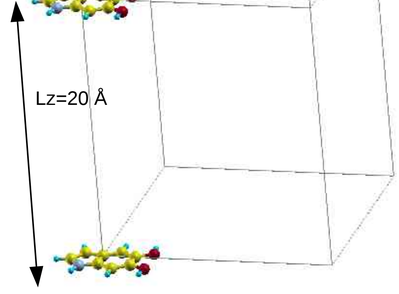




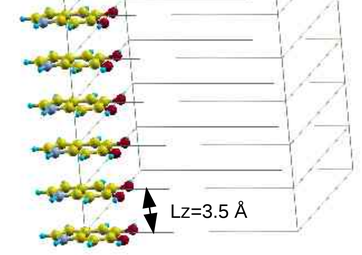




Isolated molecule



Stacking



Perspectives / further work:

Non-cofacial stacking:
- 180º or 90º – rotated molecules
- Helical stacking?

Investigate origin of spectral changes upon stacking (contributing electronic transitions...)

Different tetrameric species (HMHM, HMIM....)

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E.M. acknowledges financial support from Regione Autonoma della Sardegna (RAS) base research project CRP78744 "Energy Applications with Porous Silicon (ENAPSi)".
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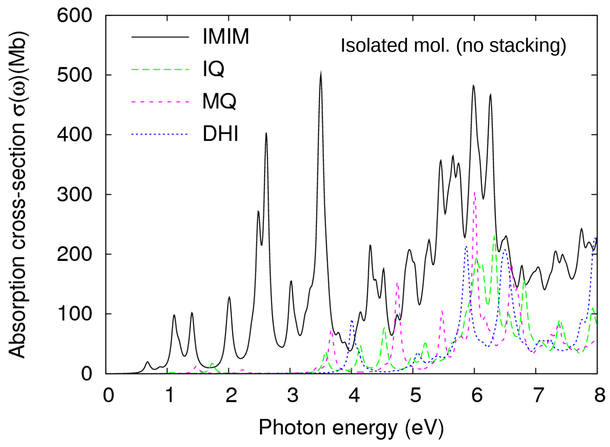
Effect of oligomerization
(tetramers vs. monomers)

IMIM tetramer



Overall redshift of main absorption peaks

Effect of stacking

Stacked case: band structure