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Eumelanin: a natural pigment for bioinspired electronics

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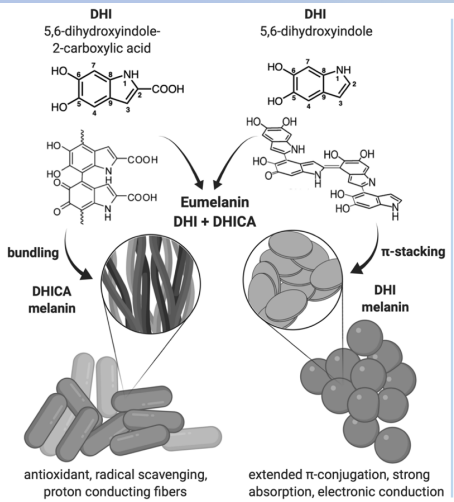
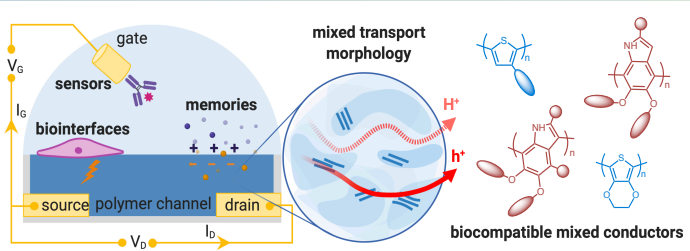


Natural eumelanin (the black pigment in our skin and hair) is made of amorphous aggregates of DHI and DHICA. These building blocks are used separately to make synthetic melanins. Due to their low solubility and chemical disorder, the structure-property relationships in eumelanin and related materials are still poorly understood.[1]

A complete structural characterization of this material is still lacking, because of its chemical complexity (tautomerisation, oxidation) and numerous conformational degrees of freedom (regio- and stereoisomers). A full understanding of the chemical and structural disorder in eumelanin and related materials is paramount to harnessing their protonic and electronic conduction.

I am leveraging DFT calculations and molecular dynamics simulations in combination with kinetics and experimental data to elucidate the chemical disorder and supramolecular organization of both DHICA and DHI melanin.

References. 1. d'Ischia, M.; Napolitano, A.; Pezzella, A.; Meredith, P.; Buehler, M. Angew. Chemie Int. Ed. 2020, 59 (28), 11196–11205. **2.** Paulsen, B. D.; Tybrandt, K.; Stavrinidou, E.; Rivnay, J. Nat. Mater. 2020, 19 (1), 13–26. **3.** Migliaccio, L.; Manini, P.; Altamura, D.; Giannini, C.; Tassini, P.; et al. Front. Chem. 2019, 7, 162. **4. Matta, M.**; Pezzella, A.; Troisi, A. J. Phys. Chem. Lett. 2020, 11 (3), 1045–1051. **5. Matta, M.**; et al.; *in preparation.*



Bioelectronic devices are novel sensing, implantable or diagnostic tools that promise to revolutionize healthcare. They use polymers able to transport both ionic and electronic charges, making them ideal to bridge the signalling gap with our cells and neurons.[2]

Existing polymers however have biocompatibility and stability issues, limiting their use in biologic media.

Eumelanin is a natural protonic and electronic conductor, and thus eumelanin-inspired polymers are promising non-cytotoxic alternatives in bioelectronics and energy storage.[3]

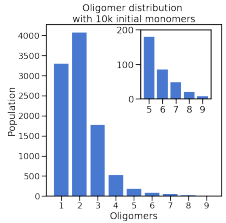
My work aims to enable the integration of eumelanin-inspired polymers in biocompatible electronics.

Unravelling the chemical complexity of DHI melanin

1. Oligomer size distribution fits a uniform growth model

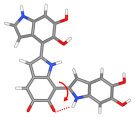
$$P_n + P_m \rightarrow P_{n+m} \qquad n, m = 1, 2, 3, \ldots$$

A kinetic 1st order model agrees with MALDI-Tof spectra obtained from solid-state oxidative polymerization. Low Mw isomers make most of the population; the low diffusivity of larger species is balanced by their higher # of reactive positions, resulting in an exponential population decay.



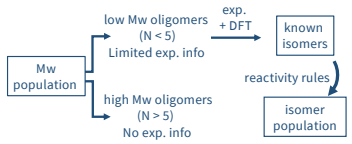
2. Oxidation is favored by new hydrogen bonds and planarization

It is estimated that 1 in 5 DHI monomers is oxidized in DHI melanin. DFT calculations on known oligomers showed the most stable oxidized isomers assume planar conformations and form intramolecular hydrogen bonds. This information will be used to generate a distribution of oxidized oligomers for higher Mw species.



2,4':2,7' trimer

3. DHI has at least 4 reactive positions; experimentally isolated species up to tetramers



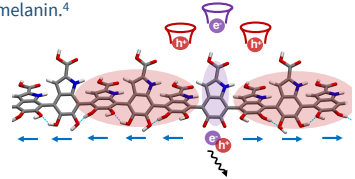
We are combining experimental information on isolated dimers, trimers and tetramers with DFT calculations to determine the likely isomer distribution of high Mw oligomers.[5]

A bottom-up model of DHICA melanin

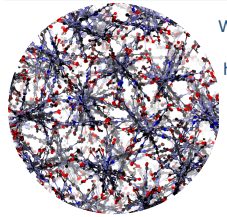
1. The photoprotective properties of DHICA are explained by strong local dipoles and oxidized oligomers

Inter-chain hydrogen bonds create strong dipoles along the polymer backbone; these localize hole charges on short chain segments. Oxidized monomers (1 in 20) create localized excited states that function as electron traps, promoting non-radiative charge recombination and thus explaining the photoprotective role of eumelanin.[4]

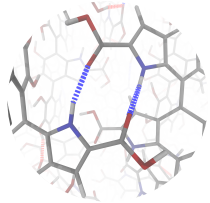
Our results suggest a viable pathway to increase delocalization is to reduce the dipole moment. This could be achieved by turning DHICA into DHI by thermal treatment.



2. Self-assembly of DHICA fibers shows promising mechanical properties



We simulated the self-assembly of DHICA melanin into fibers by arranging polymer chains in a hexagonal lattice. Our experimental collaborators are interested in obtaining electrospun DHICA fibers for biomedical applications.



DHICA's many interchain hydrogen bonds, together with the herringbone packing and torsional rigidity are expected to give these fibers a high tensile strength. We are currently characterizing their mechanical properties.[5]