Supporting Information

Size-Dependent Local Ordering in Melanin Aggregates and its Implication on Optical Properties

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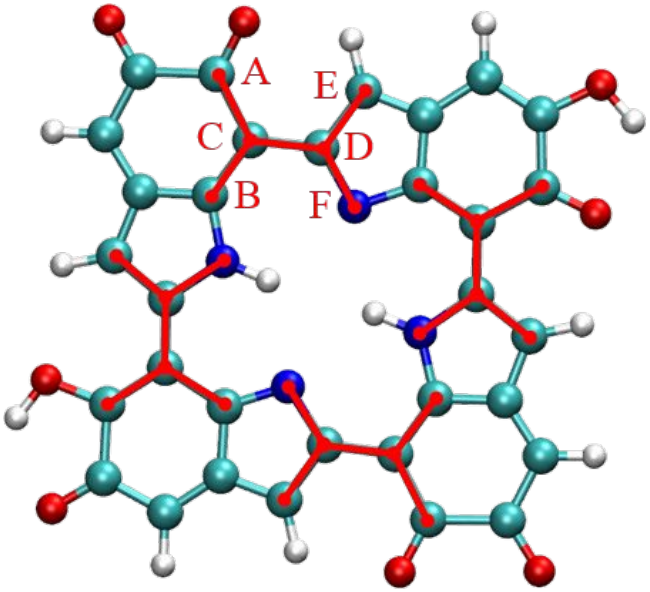
Melanin synthesis and spectra recording

The synthetic melanin based on 5,6-diacetoxyindole (DAI) was synthesized following Szpoganicz *et al*.[1]. DAI (120 mg, 0.5145 mmol) and KOH (70 mg, 1.2476 mmol) in a 20% excess per acetoxy group were stirred for 6 h in deionized water under air exposure. With this, autooxidation of the hydrolysis product 5,6-dihydroxyindole (DHI) occurs and yields the oligomerized, eumelanin-like product, indicated by a very intense black coloration. The tyrosine-based synthetic melanin was purchased from Sigma Aldrich. All chemicals were used without further purification. UV/Vis absorption spectra of diluted, aqueous solutions of the two synthetic melanin compounds were recorded with a PerkinElmer Lambda2 dual beam absorption spectrometer, a resolution of 0.5 nm, and a scan rate of 480 nm / min.

Refitted dihedral angle parameters



Dihedral:	1	2	3
½ V_n [kcal / mol]:	19.6965	5.7409	0.6427
n:	2	4	8
γ_n [°]:	180	0	180

Figure S1 / Table S1: Illustration of the refitted dihedral angles (red lines). Each of the four dihedrals A-C-D-E, A-C-D-F, B-C-D-E, and B-C-D-F across the linkage between two individual indole units is described with a series of three cosine potentials. The cosine potentials have the form $V_n(\varphi) = ½ V_n \times (1 + \cos [n \times \varphi - \gamma_n])$ with the dihedral angle φ, the barrier height V_n, the periodicity n, and the phase shift γ_n. The fitted/adjusted parameters are listed in the table above.

Aspect ratio of the two Gaussian contributions to the β-distribution

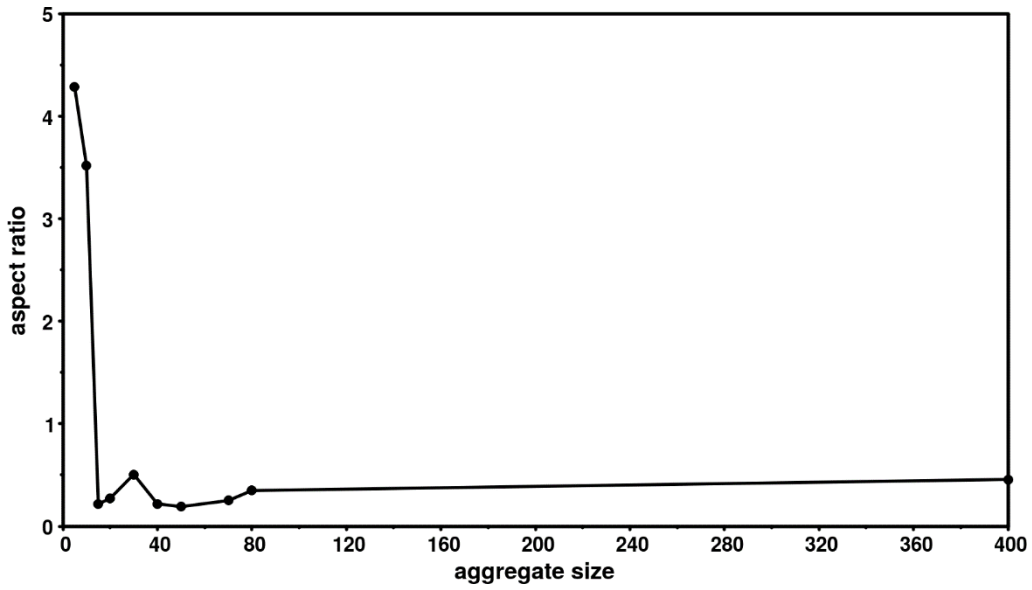


Figure S2: Aspect ratio of the two Gaussian contributions to the overall β-distribution as a function of the aggregate size. For aggregates with more than ten QIQI tetramers, the aspect ratio drops well below 1.0 and only slight changes are observed for aggregates with more than 30 QIQI tetramers.

Maximum overlap of two stacked QIQI tetramers

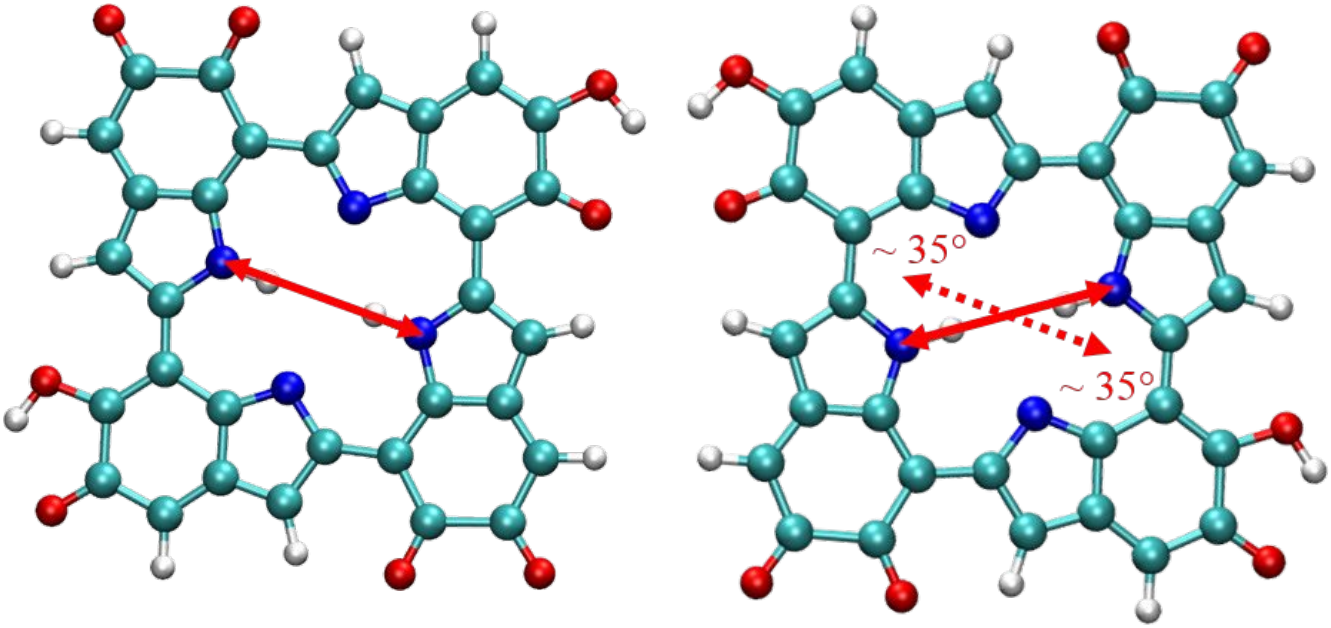


Figure S3: Illustration for the torsion angle of maximum overlap of the two QIQI tetramers. The solid red lines indicate the vectors defining the rotational orientation of each molecule. The dashed line in the right image corresponds to the solid line in the left image. The torsion angle is the sharp angle encapsulated by the solid and dashed line in the right image and is about 30° in case of antiparallel stacking with maximum overlap. It is trivial that the torsion angle of maximum overlap in case of truly parallel stacking is 0°.

Trimer spectra

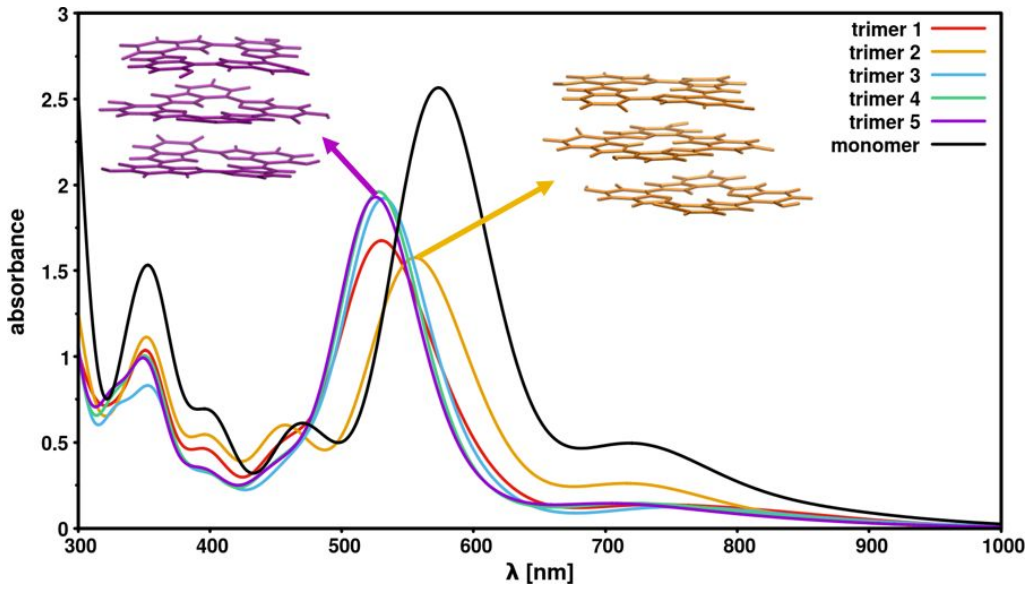


Figure S4: Calculated absorption spectra of the monomer (black line) and five different trimers (colored lines). The four structurally similar trimers #1, #3, #4, and #5 feature almost the same blue-shift relative to the monomer spectrum - which is due to their large displacement angles. Trimer #2, of which one displacement angle is much smaller than 90°, has a significantly lower blue-shift relative to the monomer spectrum. These observations for trimers are conform with the findings about dimers and pentamers discussed in the main paper.

Dimer structures

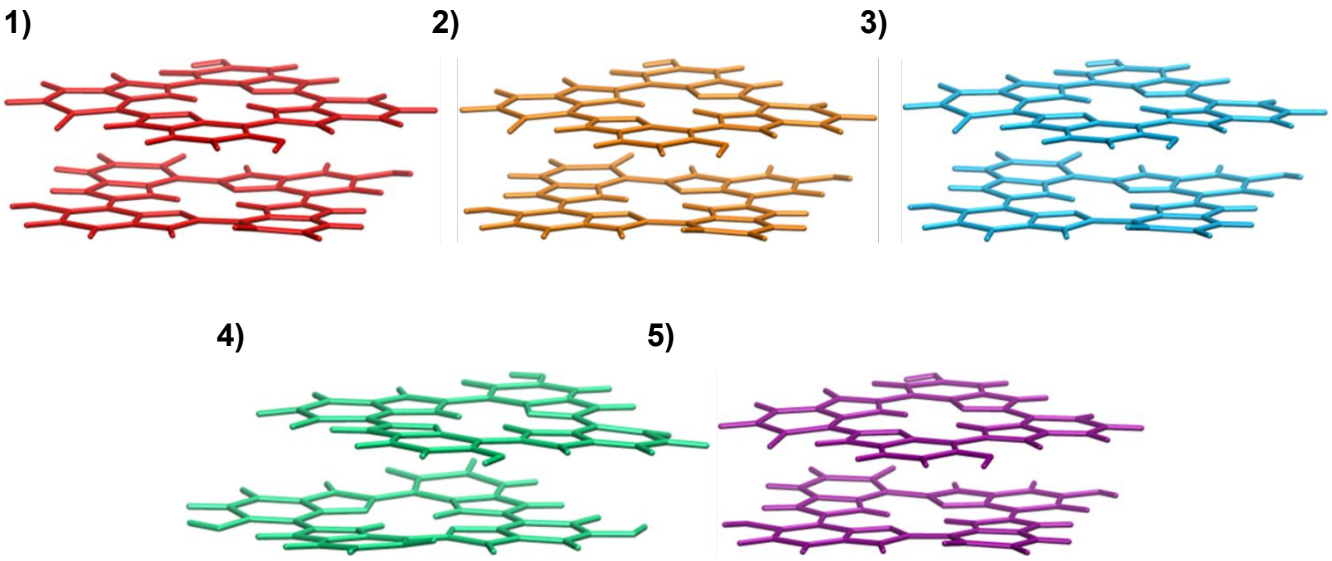


Figure S5: Structures of the five dimers of which we calculated the absorption spectra. The numbers above each structure refers to the numbering in the text. The colors correspond to the colors used to display the spectra.

Trimer structures

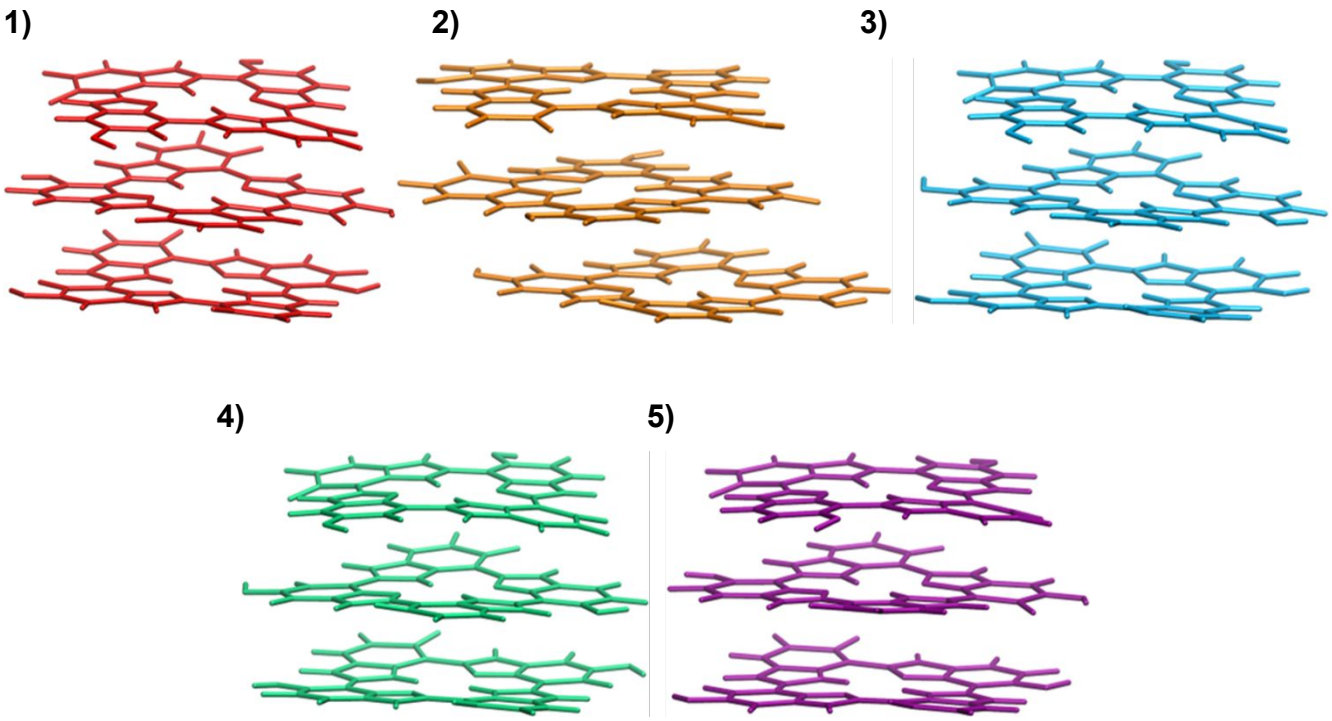


Figure S6: Structures of the five trimers of which we calculated the absorption spectra. The numbers above each structure refers to the numbering in the text. The colors correspond to the colors used to display the spectra.

Pentamer structures

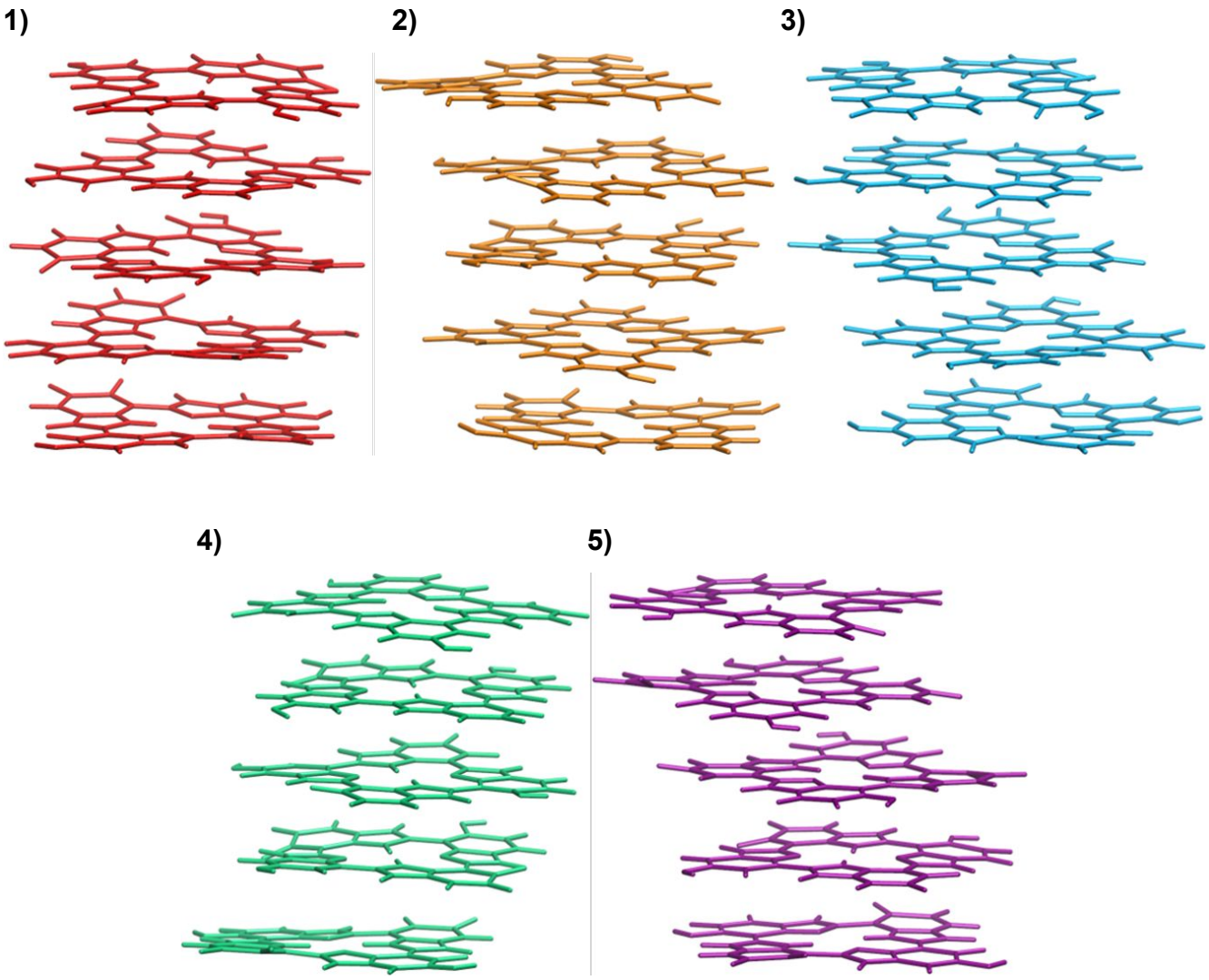


Figure S7: Structures of the five pentamers of which we calculated the absorption spectra. The numbers above each structure refers to the numbering in the text. The colors correspond to the colors used to display the spectra.

T-type aggregate structures

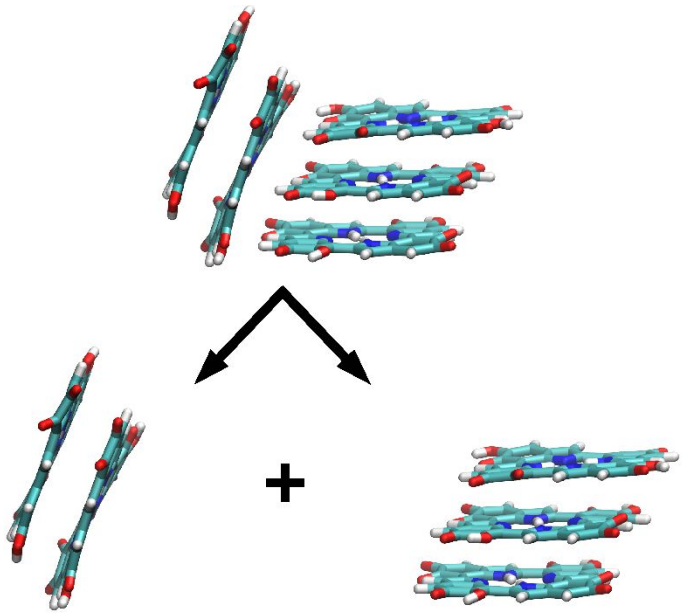


Figure S8: Structures of the T-type pentamer and its dimer and trimer components. In case of the T-type tetramer we deleted the leftmost molecule to transform the dimer into a monomer.

References:

(1) Szpoganicz B.; Gidanian S.; Kong P.; Farmer P. Metal binding by melanins: studies of colloidal dihydroxyindole-melanin, and its complexation by Cu(II) and Zn(II) ions *J. Inorg. Biochem.* **2002**, 89, 45-53.