

Supporting Information

Tuning Melanin: Theoretical Analysis of Functional Group Impact on Electrochemical and Optical Properties

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1 CO-extrusion

During the initial optimization of the synthetic melanin structure that gave the 6H-structure, CREST¹ tautomerize calculations showed that one or more of the monomeric subunits underwent a ring reduction of the six-membered rings. The energetically most favorable CO-extrusion structure is presented in Figure S1.

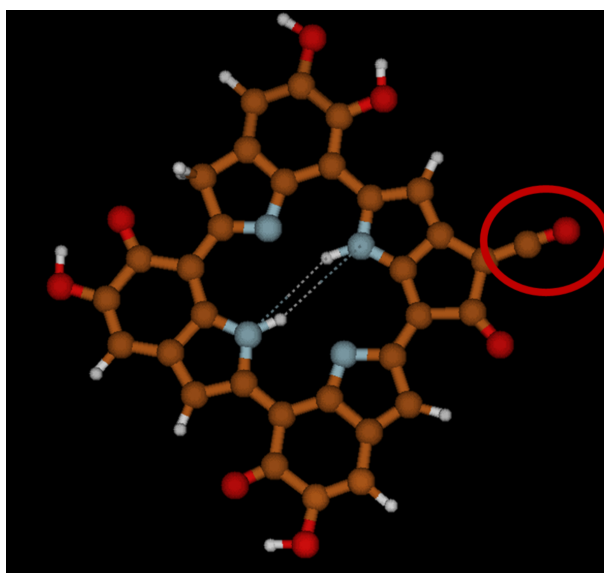


Figure S1: Example for a "CO-extrusion" (red circle) that was observed several times during the initial search for the 6H structure.

DFT calculations for the validation were performed using ORCA² on the r2SCAN-3c³ level of theory. The "CO-extrusion" structure showed comparable stability to the 6H structure (energy difference with regard to 6H tetramer of -0.52 kcal/mol) and may be of interest to further investigate in future work.

2 Semiempirical conformer search

The geometries yielded by CREST¹ calculations are presented in Figure S2.

The 6H tetramer was used as the basis structure, the substituents were added subsequently. A gfn2-xtb⁴ calculation was performed. The xtb-optimized structures were used as the input for the CREST tautomerize calculation. The positions of the oxygen atoms were fixed, otherwise it was observed that the tetramers could potentially fragment, giving energetically less stable structures. These geometries obtained from CREST were then validated by DFT calculations.

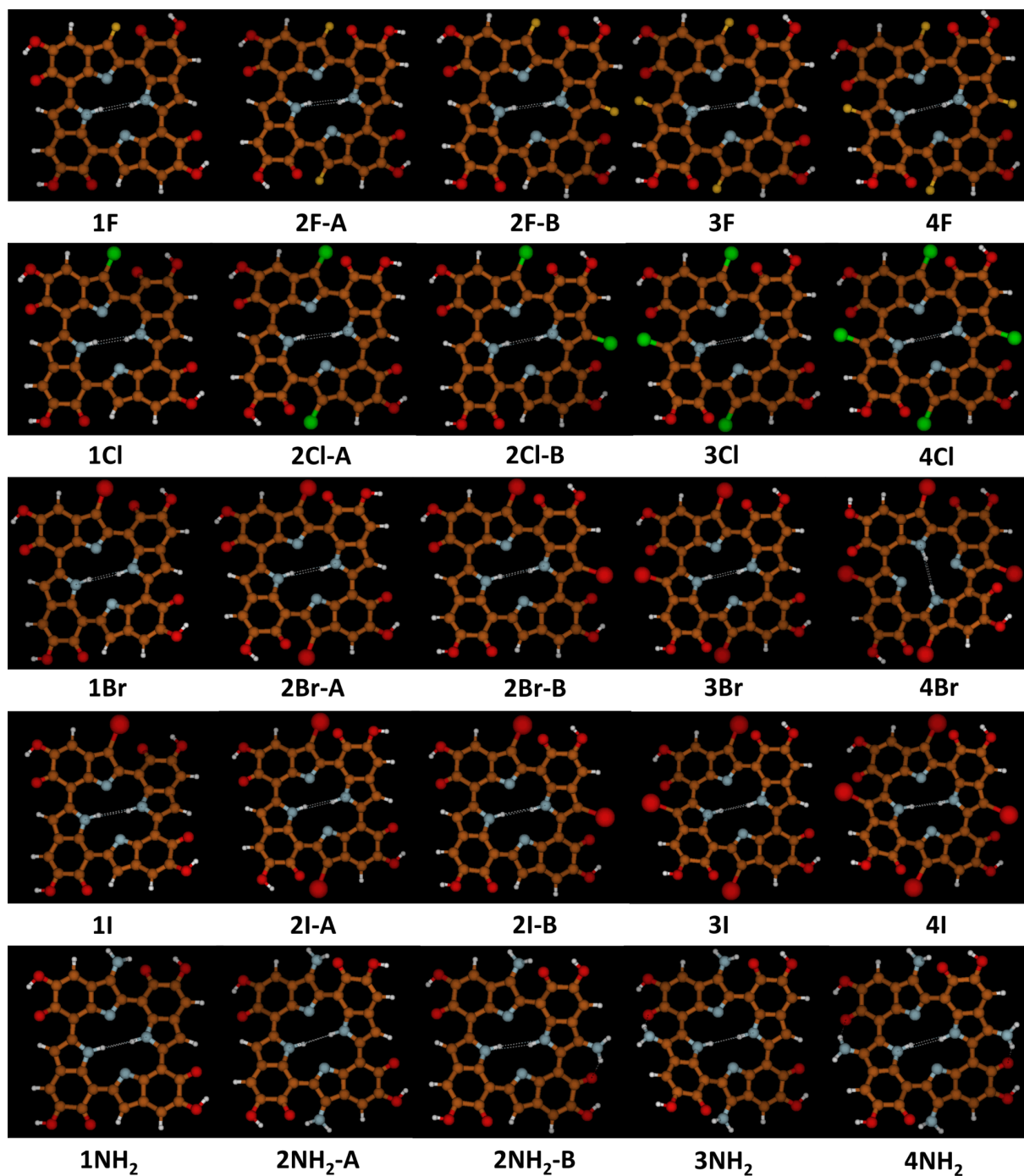


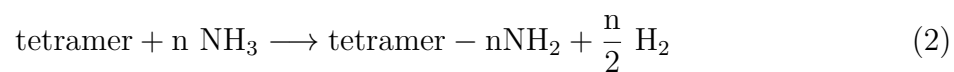
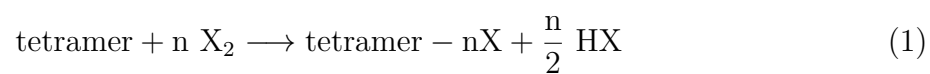
Figure S2: Geometries obtained as energetic minimum structure conformers and tautomers from CREST.

3 DFT energy evaluation

Table S1: The total energies of the melanin derivatives yielded by DFT calculations using ORCA² and the composite method r2SCAN-3C³. If no substitution pattern is given, the unsubstituted molecule was calculated.

Substituent / Molecule	Substitution Pattern	E_{tot} [Eh]	$E_{formation}$ [eV]
	1	-2147.5667	-4.40
F	2-A	-2246.7990	-8.82
	2-B	-2246.7960	-8.74
	3	-2346.0281	-13.16
	4	-2445.2572	-17.49
F ₂		-199.5141	
HF		-100.4443	
	1	-2507.9050	-0.88
Cl	2-A	-2967.4759	-1.78
	2-B	-2967.4728	-1.70
	3	-3427.0196	-1.95
	4	-3886.6118	-3.43
Cl ₂		-920.3153	
HCl		-460.7777	
	1	-4621.8642	-0.07
Br	2-A	-7195.3942	-0.16
	2-B	-7195.3910	-0.08
	3	-9768.9216	-0.19
	4	-12342.4485	-0.20
Br ₂		-5148.2626	
HBr		-2,574.7362	
	1	-2345.4614	0.83
I	2-A	-2642.5885	1.64
	2-B	-2642.5855	1.72
	3	-2939.7134	2.50
	4	-3236.8377	3.38
I ₂		-595.4866	
HI		-298.3300	
	1	-2103.6909	0.21
NH ₂	2-A	-2159.0488	0.37
	2-B	-2159.0461	0.44
	3	-2214.4032	0.62
	4	-2269.7604	0.79
NH ₃		-56.5329	
H ₂		-1.1694	
OMe	2-A	-2277.3274	
6H		-2048.3352	

The formation energies presented in Table S1 were calculated assuming the following reactions (reaction equation 1 for the halogenides, reaction equation 2 for amines).



These reactions were chosen to represent the post-polymerization conditions applied in the literature.⁵

4 Mel-OMe

In order to prove that the hydrogen bonding is responsible for the reduction of the HOMO-LUMO gap, another calculation was performed using methoxy groups as substituents. The possibility to form hydrogen bonds is a characteristic of the amine group. Substitution of opposite monomer units in di-aminated melanin shows the most pronounced decrease in the HOMO-LUMO gap. Therefore, this substitution pattern was chosen for analyzing another +M substituent, which is unable to form such hydrogen bonds, in order to analyze the potential significance of any hydrogen bond formation. Consequently, 2X-A di-substituted melanin with methoxy groups was additionally analyzed (Mel-OMe). The according minimum structure used for the calculation of the HOMO-LUMO gap is presented in Figure S3.

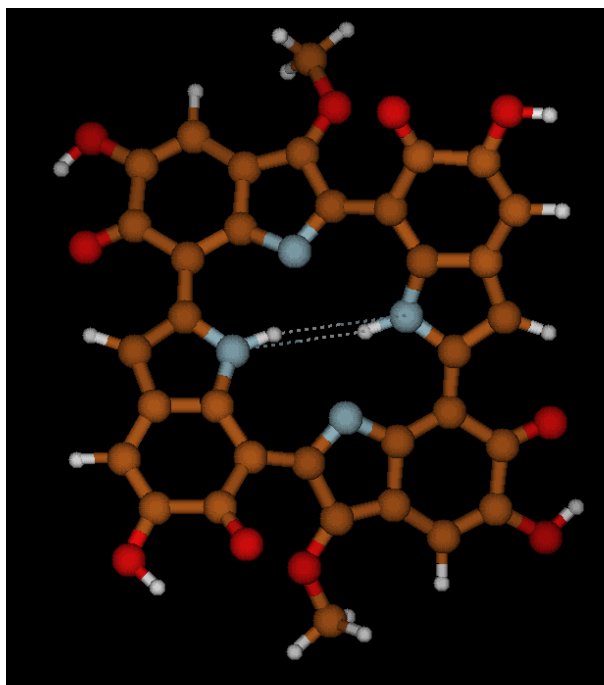


Figure S3: Geometry obtained as the energetic minimum structure conformers and tautomers from CREST for the di-substituted melanin with OMe.

5 UV-Vis spectra

UV-Vis spectra were calculated by GW-BSE calculations using MOLGW.⁶ First, a G_nW_6 calculation was performed, directly followed by a bse calculation. Both were performed on the BhLYP/cc- pVDZ(-RI)⁷⁻⁹ level of theory. The UV-Vis spectra for all five substituents and all possible degrees of substitution are presented in Figure S4-S8.

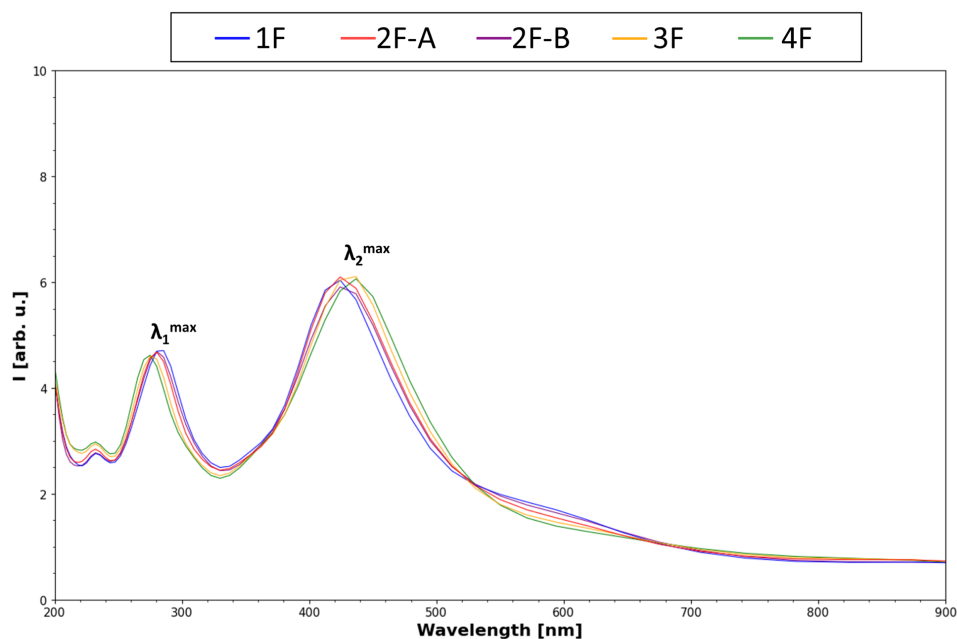


Figure S4: Calculated UV-Vis spectra for Mel-F, obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

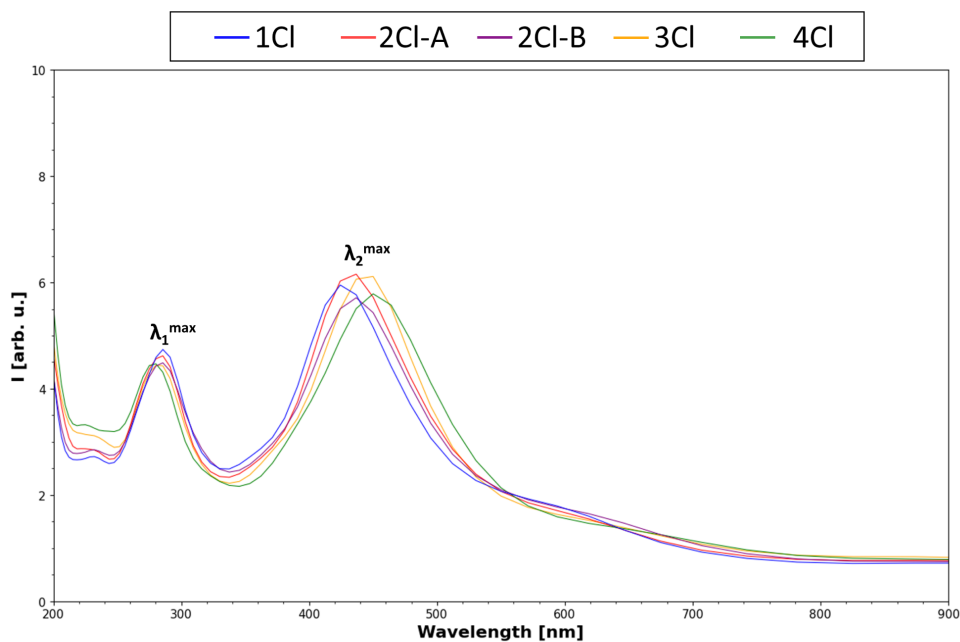


Figure S5: Calculated UV-Vis spectra for Mel-Cl, obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

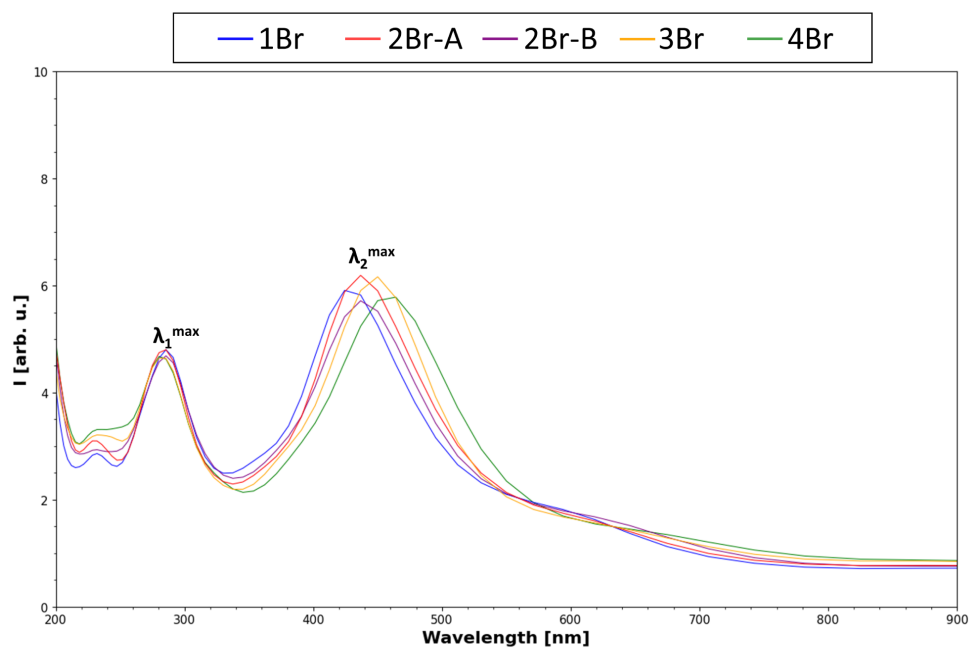


Figure S6: Calculated UV-Vis spectra for Mel-Br, obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

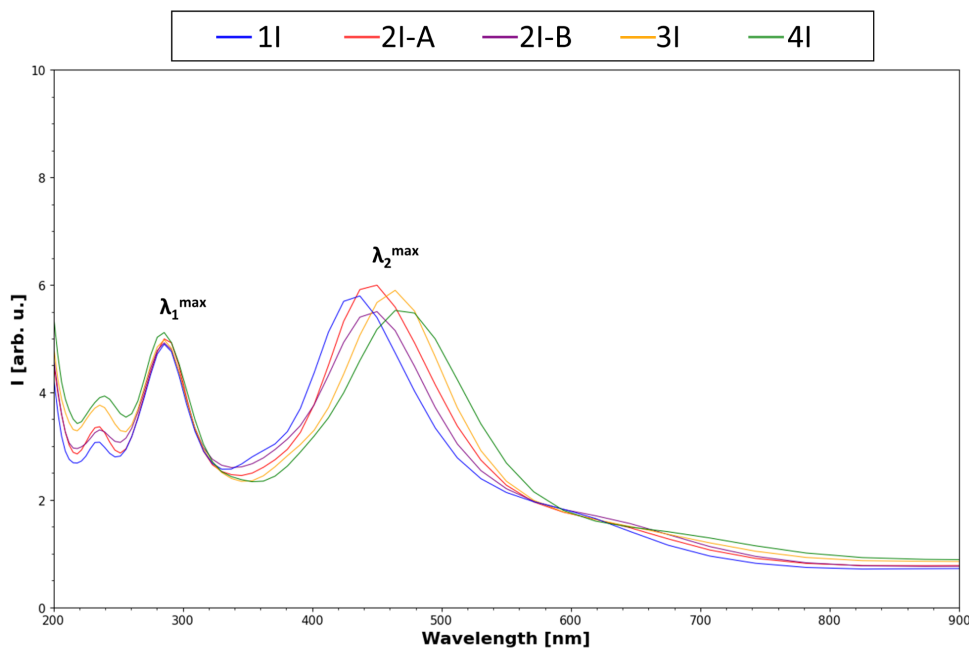


Figure S7: Calculated UV-Vis spectra for Mel-I, obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

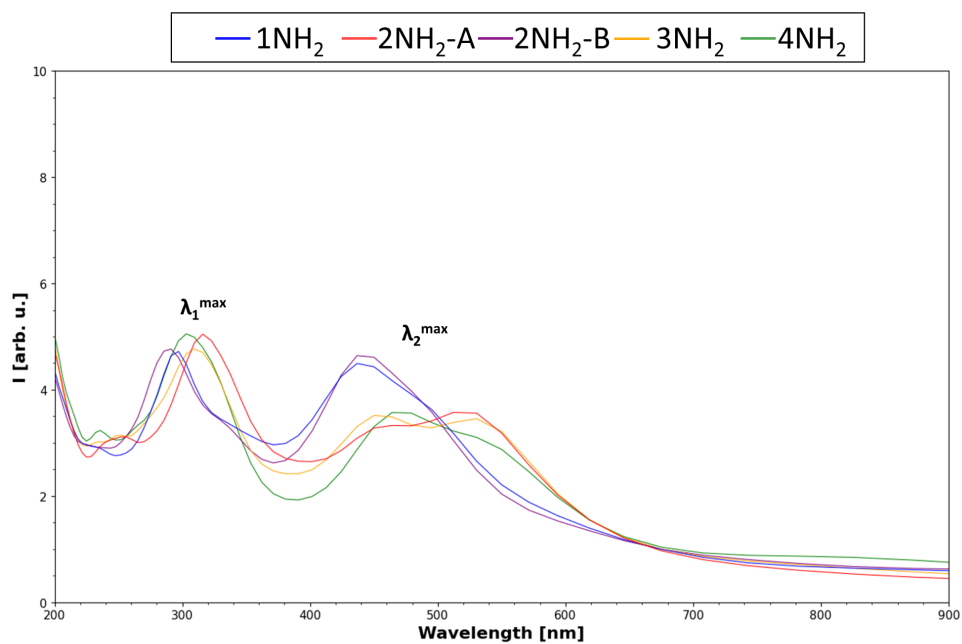


Figure S8: Calculated UV-Vis spectra for Mel-NH₂, obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

Additionally, the wave length of both peaks visible in all of the calculated spectra are presented in Table S2.

Table S2: Peak positions of both peaks visible in all calculated spectra. The spectra were obtained from GW-BSE calculations on the BhLYP/cc-pVDZ(-RI)⁷⁻⁹ level of theory.

Substituent	Substitution Pattern	λ_1^{max}	λ_2^{max}
F	1	285.64	424.38
	2-A	280.25	424.38
	2-B	280.25	424.38
	3	275.06	436.86
	4	275.06	436.86
Cl	1	285.64	424.38
	2-A	285.64	436.86
	2-B	285.64	436.86
	3	280.25	450.10
	4	280.25	450.10
Br	1	285.64	424.38
	2-A	285.64	436.86
	2-B	285.64	436.86
	3	280.25	450.10
	4	280.25	464.17
I	1	285.64	436.86
	2-A	285.64	450.10
	2-B	285.64	450.10
	3	285.64	464.17
	4	285.64	464.17
NH ₂	1	297.07	436.86
	2-A	316.03	512.18
	2-B	291.24	436.86
	3	309.44	450.10
	4	303.13	464.17

6 Comparison of Mel-NH₂ and Mel-OMe

Additional geometries of the obtained 2X-A di-substituted Mel-NH₂ and Mel-OMe structures are presented in Figure S9. This substitution pattern was chosen because it showed the biggest decrease in the HOMO-LUMO gap in the case of aminated melanin.

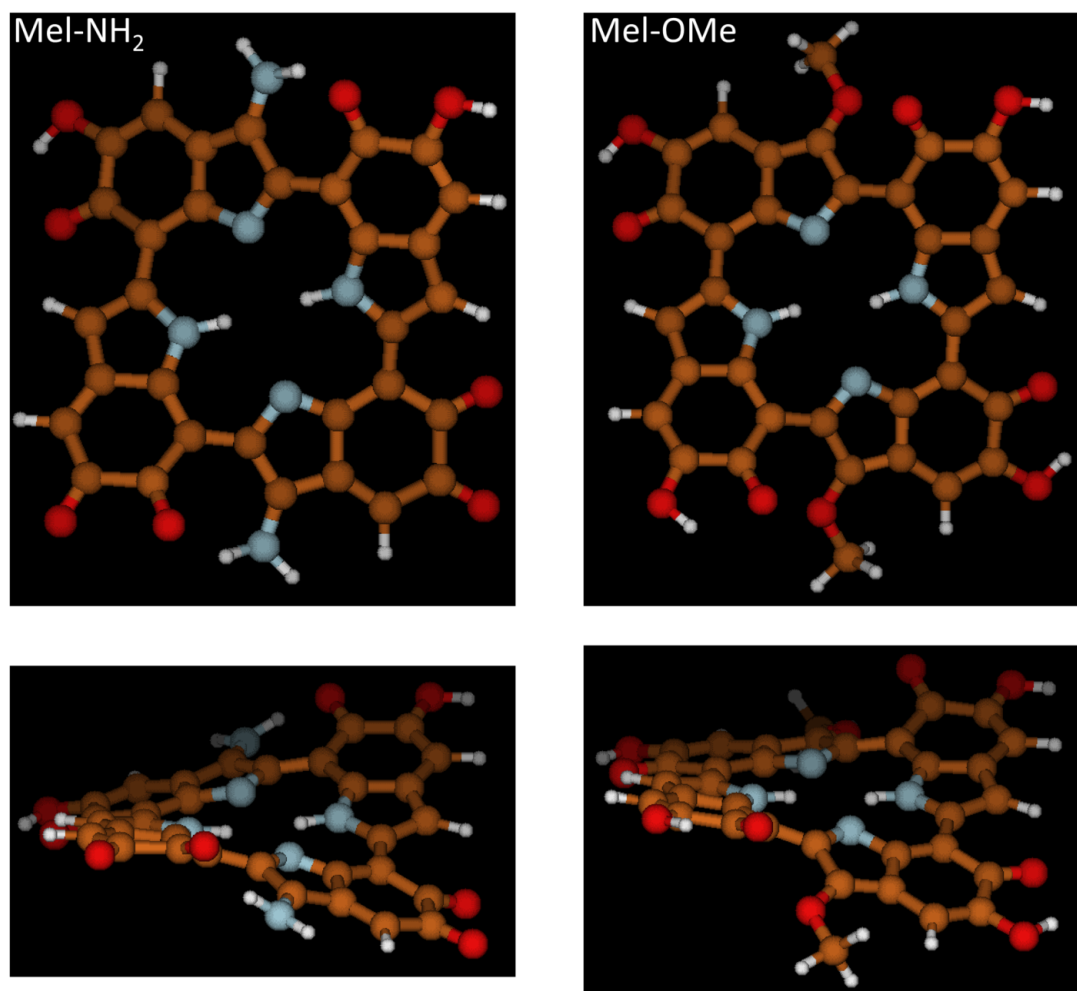


Figure S9: Obtained geometries for 2X-A di-substituted Mel-NH₂ (on the left, top and side view) and 2X-A Mel-OMe (on the right, top and side view).

A loss of planarity is observed in both structures and a clear similarity in the geometries is visible. Despite both structures exhibiting this loss of planarity, there is no similar reduction in the HOMO-LUMO gap in the case of OMe as the substituent. Therefore, we conclude that hydrogen bonding is likely the primary contributing factor for decreasing the HOMO-LUMO gap.

References

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