Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electron Supplementary Information for:

Theoretical Insights into the Photo-protective Mechanisms of Natural Biological Sunscreens: Building Blocks of Eumelanin and Pheomelanin

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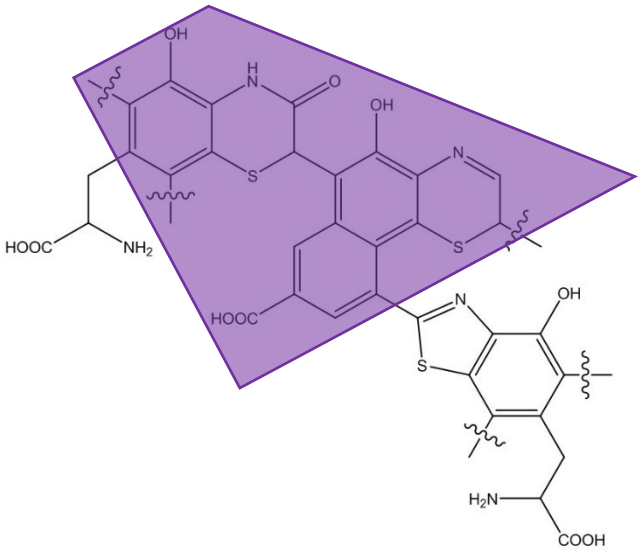
Fig. S1.1: Full repeating molecular structure of pheomelanin.



The above shows the section through the repeating molecular structure of pheomelanin. The purple area represents the focal section through which the present study was based on.

Fig. S1.2: Various low energy ground state isomers of the trimeric unit of EU.

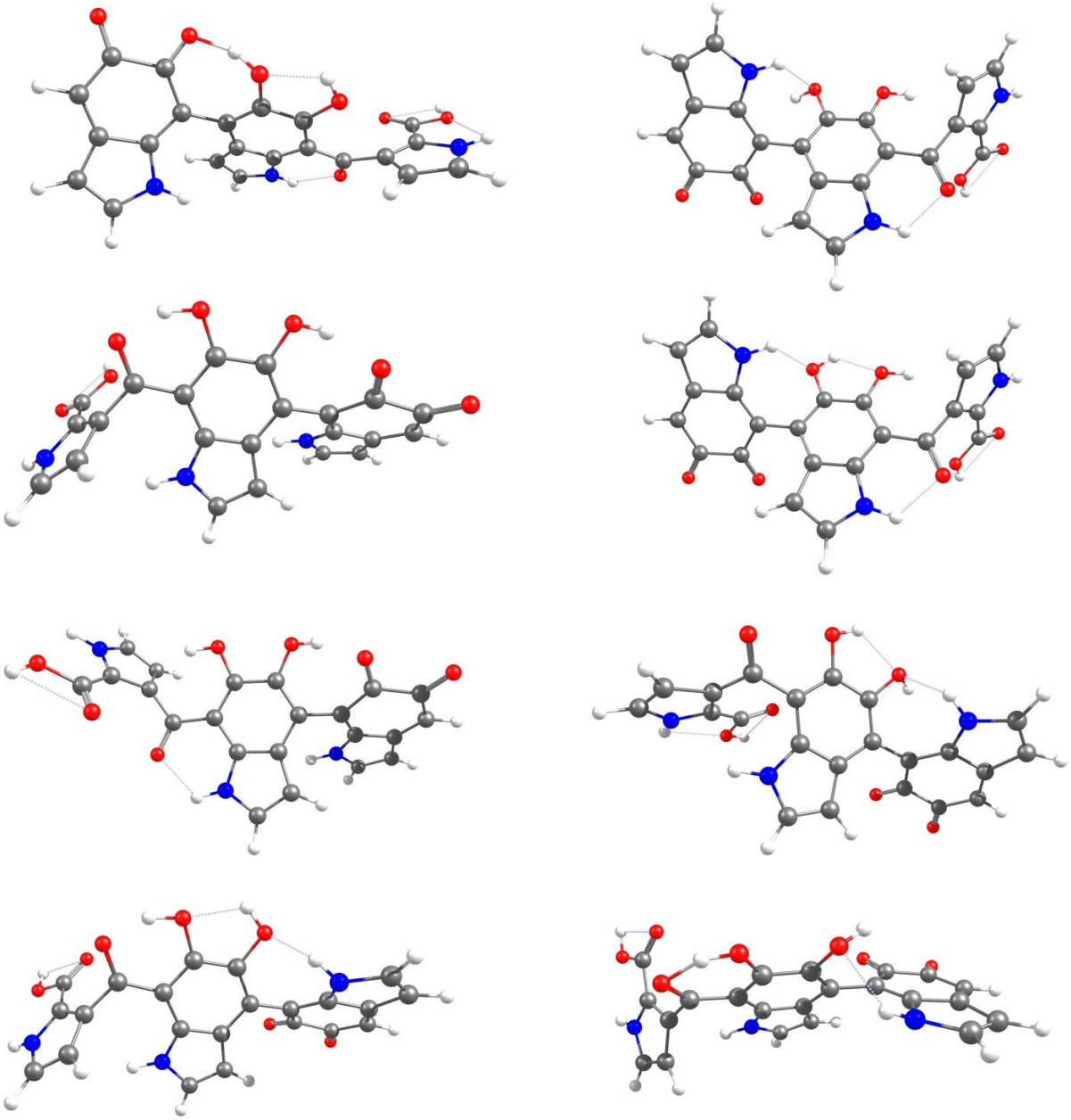


Fig. S2.1: Orbitals and orbital promotions of the other structures of EU not displayed in fig. 2 of the main paper.

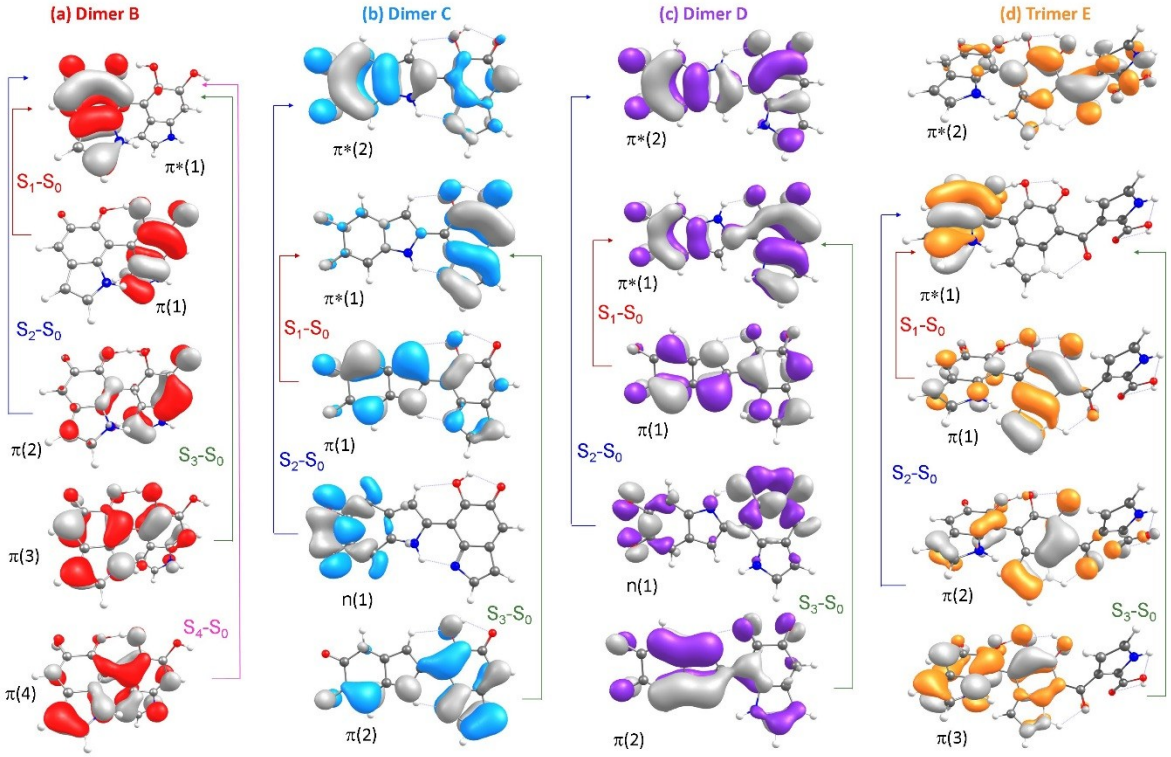


Fig. S2.2: Cumulative continuous spectrum (grey profile) constructed by fitting individual Gaussian functions (of FWHM = 100 nm) to the calculated vertical excitation energies of structures A-F of EU.

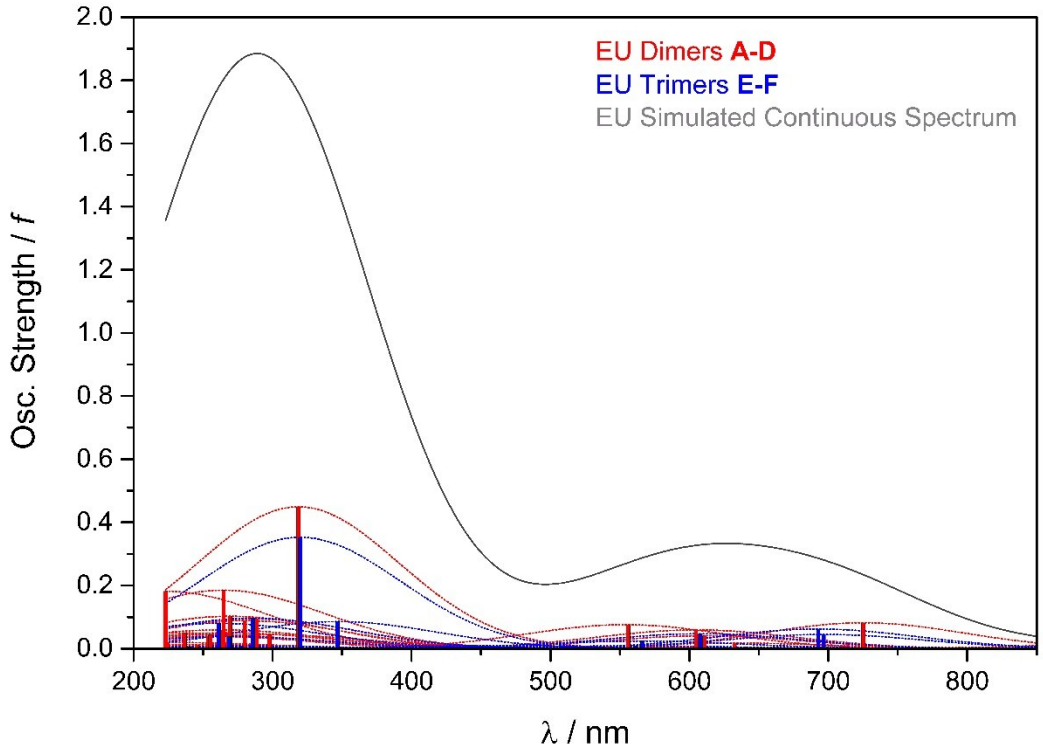


Fig. S2.3: The Orbital promotion accompanying the S_1(CT) state of Dimer D at $R_{O\text{-}H}$ = 1.0 Å.

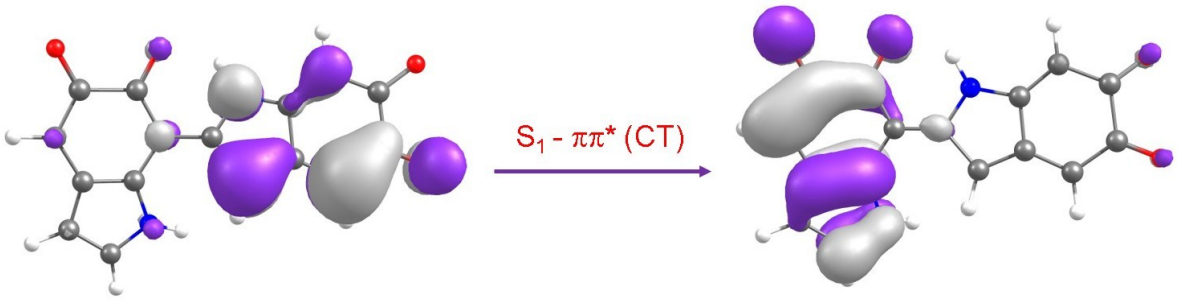


Fig. S3.1: Benchmark PE profiles of Dimer A calculated at the CASPT2(6,6)/cc-pVDZ level of theory. The filled black circles indicate the optimised geometry of the ground state at a particular $R_{O\text{-}H}$ distance. The open red circles represent the vertical excited energies at a given $R_{O\text{-}H}$ relaxed geometry.

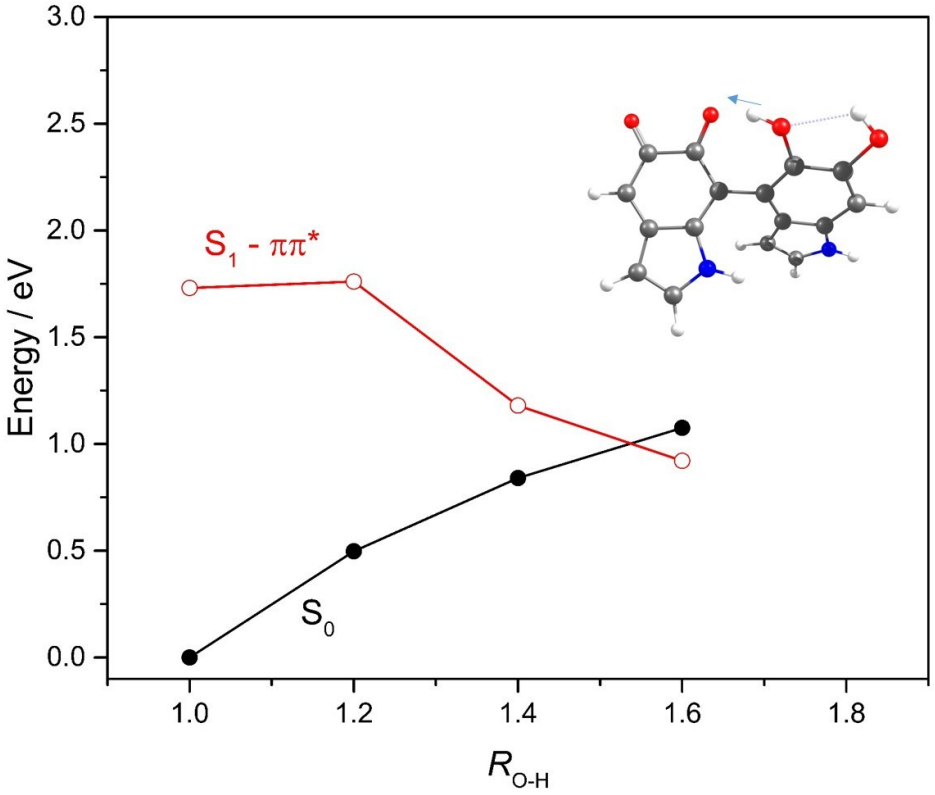


Fig. S3.2

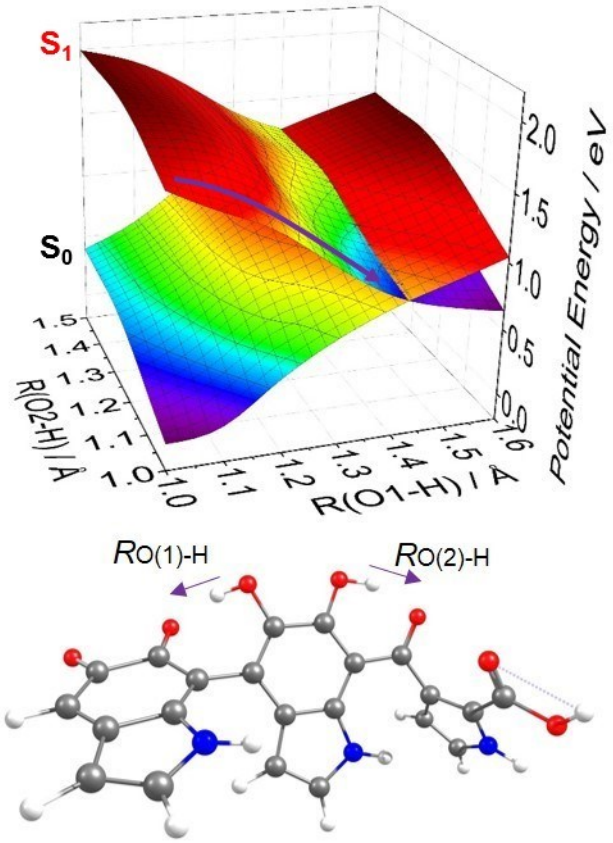
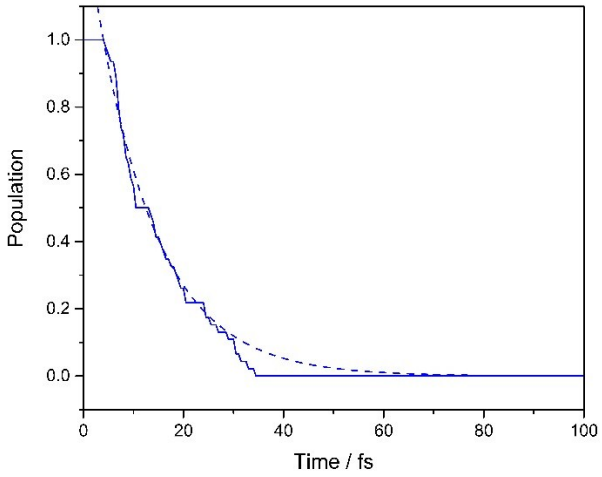


Fig. S4: Decay profile of Dimer A obtained by calculating the energies and gradients using TD-B3LYP/cc-pVDZ.



The decay profile was fitted to equation 1 of the main paper - returning an S_1 lifetime of 16 fs.

Table S1: Comparison of vertical excitation energies derived using TDDFT and ADC(2).

Electronic Transition	ADC(2) / cc-pVDZ	TD-B3LYP / 6-31G	TD-B3LYP / cc-pVDZ
Dimer A of EU			
S_1-S_0	1.78 (0.0537) – ππ*(CT)	1.13 (0.0112) – ππ*(CT)	1.19 (0.0070) – ππ*(CT)
S_2-S_0	2.03 (0.0405) – ππ*	1.27 (0.0315) – ππ*	1.32 (0.0363)
S_3-S_0	2.29 (0.0062) – ππ*	1.85 (0.0315) – ππ*	1.88 (0.0103
PM			
S_1-S_0	3.57 (0.0799) - ππ*	3.20 (0.0810) - ππ*	-
S_2-S_0	3.86 (0.1181) - ππ*	3.37 (0.0785) - ππ*	-
S_3-S_0	4.17 (0.0075) - ππ*	3.54 (0.0175) - ππ*	-

Table S2: S_1 lifetimes returned using varying values of $\Delta E(S_1\text{-}S_0)$.

$\Delta E(S_1\text{-}S_0)$ / eV	Lifetime (τ) / fs
Dimer A of EU	
0.10	15
0.13	12
0.15	10
PM	
0.10	59
0.13	55
0.15	50