Supporting Information

Stability and Optical Absorption of a Comprehensive Virtual Library of Minimal Eumelanin Oligomer Models**

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SI1. **Classification scheme**

SI1.1 **Resonance/bonding classification**

The resonance/bonding dimer classification is based on the fragment library shown in Schemes SI1 and SI2. The monomer fragments (MF) are classified as MF-nH, where \( n \) is the number of oxidized sites, and labelled as \( b \)-n.ijk, where \( b \) is the bond connectivity at the bonding site, \( n \) the bonding site, and ijk codifies whether the N, O5 or O6 sites are reduced (digit=0) or oxidized (digit=1). In the cyclic structures where one of the heteroatoms is bonded, the corresponding digit is set to x. All linear and cyclic MF-0H and MF-2H fragments can be described by neutral resonance structures with single-bond connectivity at the connecting site(s), and are labeled s. In contrast, the MF-1H and MF-3H fragments can be described either by neutral resonance structures with double-bond connectivity at the connecting site(s), which are labeled d, or by zwitterionic resonance structures labeled z. The rules for the dimers are that two s fragments give an s dimer; two d fragments give a d dimer; and two z fragments or one d and one z fragment give a z dimer.

![Scheme SI1](image-url)
We introduce an unambiguous, specific nomenclature that describes the structural features in a compact way. For the linear structures, the name has the form \( r \text{.} \text{lin} \text{.} \text{mn} \text{.} x \text{.} abc \text{.} def \). The meaning of each string is as follows:

- \( r \) (resonance/bonding key): \( s \) (interfragment single bond); \( d \) (interfragment double bond) or \( z \) (zwitterionic)
- \( \text{lin} \): linear dimer
- \( u \) (stereochemistry of the interfragment bond): \( c \) (cis) or \( t \) (trans)
- \( mn \): numbering of the carbons forming the interfragment bond
- \( x \): total oxidation state of the dimer
- \( abc\text{-}def \) (oxidation state of \( N_1 \), \( O_5 \) and \( O_6 \) of the first and second fragment, respectively): 0 (reduced) or 1 (oxidized)

For the cyclic structures, the format is \( r \text{.} \text{cyc} \text{.} \text{mn} \text{.} op \text{.} x \text{.} abc\text{-}def \), where the meaning is:

- \( r \) (resonance/bonding key): \( s \) (two interfragment single bonds); \( d \) (one or two interfragment double bond) or \( z \) (zwitterionic)
• *lin*: cyclic dimer
• *mn.op*: numbering of the carbons forming the two interfragment bonds
• *x*: total oxidation state of the dimer
• *abc-def* (oxidation state of N₁, O₅ and O₆ of the first and second fragment, respectively): 0 (reduced), 1 (oxidized) or X (involved in interfragment bond)

Some examples of nomenclature are given in Table SI2.

**Table SI2.** Illustration of the nomenclature for relevant structures from Schemes 1 and 2.

| Structure | Resonance/ bonding key | Linear/ cyclic | cis/ trans | Atom connectivity | Total oxidation state | Oxidized sites first ring | Oxidized sites second ring |
|-----------|------------------------|---------------|------------|-------------------|-----------------------|---------------------------|---------------------------|
| HO\(\text{N}H\)\(\text{OH}\) | s (interfragment single bond) | lin | t | 22 | 0 | 000 | 000 |
| HO\(\text{N}H\)\(\text{OH}\) | d (interfragment double bond) | lin | c | 22 | 1 | 001 | 001 |
| HO\(\text{N}H\)\(\text{OH}\) | z (zwitterionic) | lin | t | 23 | 1 | 001 | 001 |
| HO\(\text{N}H\)\(\text{OH}\) | s (interfragment single bond) | lin | c | 27 | 2 | 011 | 011 |
| HO\(\text{N}H\)\(\text{OH}\) | d (interfragment double bond) | lin | c | 27 | 2 | 001 | 111 |
| HO\(\text{N}H\)\(\text{OH}\) | s (interfragment single bond) | cyc | - | 34.43 | 0 | 000 | 000 |
### Computational details

#### SI2.1 Choice of electronic structure method

The calculations (ground-state optimizations and excited-state single point calculations) were carried out with density functional theory (DFT), using the CAM-B3LYP functional and the 6-311G(d,p) basis set. This choice is based on the good performance of CAM-B3LYP for the excited-state calculations\(^1\) since it avoids spurious charge transfer stabilization effects\(^2\) that are likely to occur in the dimers with other functionals such as B3LYP. The performance of CAM-B3LYP for the ground-state optimizations was benchmarked against MP2/cc-pVTZ for the reduced dimers (see SI2.1.1). Solvent effects were taken into account with the SMD continuum model\(^3\) using water as solvent. All calculations were performed with Gaussian 16\(^4\).

In addition to the 830 reported compounds, we considered six more isomers that were discarded, two because the structure is not stable (optimization led to a different structure after tautomerization, see SI2.1.2) and four because the restricted DFT wave function had an instability indicative of radical character (see SI2.1.3). For every optimized structure, the vertical absorption energy and oscillator strength of the three

\[\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Structure} & \text{Type} & \text{Bond} & \text{Charge} & \text{Absorption Energy} & \text{Oscillator Strength} \\
\hline
d.cyc.34.43.1.010-100 & d (interfragment double bond) & cyc & - & 34.43 & 1 & 010 & 100 \\
\hline
d.cyc.17.43.1.x10-100 & d (interfragment double bond) & cyc & - & 17.43 & 1 & x10 & 100 \\
\hline
z.cyc.34.43.1.010-010 & z (witterionic) & cyc & - & 34.43 & 1 & 010 & 010 \\
\hline
s.cyc.34.43.2.011-011 & s (interfragment single bonds) & cyc & - & 34.43 & 2 & 011 & 011 \\
\hline
d.cyc.34.43.3.111-111 & d (interfragment double bond) & cyc & - & 34.43 & 3 & 111 & 111 \\
\hline
\end{array}\]
lowest excited states is calculated with linear-response time-dependent DFT (TD-DFT). The suitability of TD-CAM-B3LYP was assessed comparing the vertical excitations of the reduced and oxidized monomers with MS-CASTP2 and EOM-EE-CCSD literature values.\cite{5} The differences are approximately 0.2 eV, which lies in the expected precision range for TD-CAM-B3LYP (see SI2.1.4).

**SI2.1.1 Benchmark of ground-state approach**

The validity of our approach to estimate the stability of the different compounds was tested for the set of 20 linear, fully reduced DHI dimers. As a benchmark method we used MP2 with Dunning's correlation-consistent polarized valence triple-z (cc-pVTZ) basis set and SMD solvation. We considered SMD-CAM-B3LYP/6-311G(d,p) with and without the atom-pair wise dispersion D3 correction\cite{6} and SMD-B3LYP/6-311G(d,p) for reference, and compared the relative potential energies of the 22 compounds with the three approaches. The results are shown in Figure SI1, where we display the relative energies following the MP2 energies in decreasing order. In the plots the blue and red bars represent MP2 and DFT energies, respectively. The relative energies span a range of 10 kcal·mol\(^{-1}\) with MP2. The CAM-B3LYP energies are somewhat less dispersed, but the range of dispersion is closer to MP2 when the D3 correction is not included (6 vs 4 kcal·mol\(^{-1}\), Figures SI1a and SI1b). In addition, the order of the compounds is approximated better with CAM-B3LYP than by CAM-B3LYP-D3. In particular, CAM-B3LYP-D3 clearly underestimates the relative energies of the c.77 and c.47 isomers, which are the less stable ones at the MP2 level and the second and fourth more stable ones with CAM-B3LYP-D3. The root mean square of the difference (RMSD) between the relative energies is 3.1 kcal/mol for CAM-B3LYP and 5.0 kcal/mol for CAM-B3LYP-D3. Overall, the agreement with MP2 is better without the D3 correction. Therefore, the D3 scheme was discarded. Uncorrected B3LYP (see Figure SI1c) has a smaller RMSD for the benchmark set, 1.8 kcal/mol, but given that the difference between CAM-B3LYP and B3LYP is only 1.3 kcal/mol, we have chosen CAM-B3LYP for the optimizations to be consistent with the excited-state calculations. The good agreement between CAM-B3LYP and MP2 is also seen comparing the energy distribution histograms as a function of the type (Figure SI2).
Figure SI1. Relative potential energy of the Ox0-lin compounds calculated at the MP2/cc-pvtz level (blue bars) compared with DFT (red bars): CAM-B3LYP/6-311G** without and with the D3 correction, and B3LYP/6-311G** (panels (a), (b) and (c), respectively).
Figure SI2. Energy distribution of Ox0-lin isomers as a function of their type calculated with MP2/cc-pvtz and CAM-B3LYP/6-311G** (upper and lower panels, respectively).
SI2.1.2 Unstable tautomers
Two structures (z.lin.t.47.1.010-010 and z.lin.c.77.1.100-010) were not stable towards interfragment tautomerization. Upon optimization, they yielded structures z.lin.t.47.1.000-110 and z.lin.c.77.000-110, respectively. The unstable isomers were not included in the library.

SI2.1.3 Wave function stability of z structures
The structures with z resonance/bonding character may be prone to have a diradical character that makes them unsuitable for our theoretical approach. This possibility was examined reoptimizing all z structures with unrestricted CAM-B3LYP and comparing the results with the restricted approach. Four structures (z.lin.c.37.1.001-010, z.lin.c.37.1.010-001, z.lin.t.37.1.100-010 and z.lin.t.44.1.010-001) give a lower energy minimum with unrestricted CAM-B3LYP, which is indicative of instability of the restricted wave function and possible radical bicharacter. The structures were therefore discarded.

SI2.1.4 Benchmark of excited-state approach
The suitability of TD-CAM-B3LYP for the vertical excitations is assessed comparing the vertical excitations of the DHI, IQ and NQ monomers in the gas phase with high-level EOM-EE-CCSD and MS-CASPT2 calculations from Ref. [7] (Table SI1). TD-DFT excitations in solution are given in the fifth column. The differences of gas-phase TD-DFT with respect to EOM-EE-CCSD are 0.16 - 0.23 eV, and those with respect to MS-CASPT2 0-16 - 0.28 eV, ie overall there is a difference of approximately 0.2 eV which lies within the expected precision range of TD-CAM-B3LYP. Note that inclusion of solvation effects has a substantial effect on the excitation energies of IQ and NQ (decrease by approximately 0.2 eV) because of an increase in the dipole moment upon excitation.

Table SI1. Vertical S1 excitation energy [eV] of the DHI monomer and the oxidized IQ and NQ forms calculated at different levels of theory.

|       | EOM-EE-CCSD/6-311++G(d,p) | MS-CASPT2/6-311++G(d,p) | TD-CAM-B3LYP/6-311G(d,p) | TD-CAM-B3LYP/6-311G(d,p) |
|-------|--------------------------|-------------------------|--------------------------|--------------------------|
| DHI   | 4.55                     | 4.58                    | 4.78                     | 4.79                     |
| IQ    | 2.33                     | 2.43                    | 2.15                     | 1.92                     |
| NQ    | 2.37                     | 2.05                    | 2.21                     | 2.04                     |

aGas phase, Ref. [7]. bGas phase, this work. cSolution (SMD), this work.

SI2.2 Calculation of free energy
The free energy G of the different compounds is the free energy in solution at 298 K including translational, rotational, and vibrational contributions, and the electronic contribution for O2. To save computational effort, the vibrational contribution of the dimers has been obtained from the SMD calculated frequencies for representative structures, namely the most stable cyclic and linear isomer of all oxidation states, and the same contribution has been used for all cyclic or linear isomers of the same oxidation state. Similarly, for all dimers the rotational entropy is approximated using the moments of inertia of the representative structures mentioned above. Following Eq. 6a of Ref. [8], for the Gibbs translational free energy correction \( T \cdot S_{tr} \), the translational entropy is calculated using the free solvent volume of water with an intermediate value of 7 for
the $C_{\text{free}}$ constant. For the dimers and water we assume standard conditions ($\alpha_X = 1$), while for oxygen we assume an activity of $2.5 \times 10^{-4}$, which corresponds to the solubility of oxygen in water at 298 K (8 mg·L$^{-1}$)$^9$. The latter term is included as $RT \cdot \ln(\alpha_X)$ in $G(O_2)$.

**SI2.3 Thermodynamic scheme to balance stoichiometry**

To compare the energy of dimers with different stoichiometry, we consider that the oxidation proceeds with ground-state (triplet) oxygen, as in one of the common methods of dopa polymerization.$^{10}$ In this case, it is possible to compare the energy of isomers of different stoichiometry with the following equation, where the oxidation is balanced with $O_2$ and $H_2O$ molecules (Equation S1):

$$C_{16}H_{12}N_2O_4 + \frac{m}{2} O_2 \rightarrow C_{16}H_{12-2m}N_2O_4 + m H_2O$$  \[S1\]

In Equation S1, $C_{16}H_{12}N_2O_4$ is the stoichiometric formula of the fully reduced linear dimers (oxidation state 0). Using Equation S1, the energy of dimers with different composition can be compared calculating the following energy, which we term $G^*$ (Equation S2):

$$G^*_{C_{16}H_{12-2m}N_2O_4} = G_{C_{16}H_{12-2m}N_2O_4} + mG_{H_2O} - (m/2)G_{O_2}$$  \[S2\]

The linear dimers with oxidation state 0, 1, 2 and 3 correspond to $m = 0, 1, 2$ and 3. As for the cyclic dimers, they have 2 hydrogen atoms less than the linear counterparts. Therefore, cyclic dimers with oxidation state 0 - 3 have $m = 1 - 4$.

**SI3. Full histograms of energy distribution**

![Figure SI3. Free energy distribution of (a) linear and (b) cyclic dimers as a function of their oxidation state, relative to the most stable library dimer (cf Figure 1).](image-url)
Figure SI4. Free energy distribution of linear isomers as a function of type. Compounds are grouped by oxidation state, and energies are relative to the most stable dimer of each group (cf Figure 2).
Figure SI5. Free energy distribution of cyclic isomers as a function of type. Compounds are grouped by oxidation state, and energies are relative to the most stable dimer of each group (cf Figure 3).
SI4. **Most stable linear isomers of each connectivity**

**Table SI2.** Most stable linear isomers of each connectivity.

| Connectivity | Most stable isomer      | Oxidation state | ΔG [kcal·mol⁻¹]ᵃ |
|--------------|-------------------------|-----------------|-----------------|
| 22           | s.lin.t.22.2.011-011    | 2               | -30.7           |
| 23           | d.lin.t.23.2.001-111    | 2               | -18.5           |
| 24           | d.lin.c.24.2.001-111    | 2               | -19.2           |
| 27           | d.lin.t.27.2.001-111    | 2               | -26.0           |
| 33           | d.lin.t.33.3.111-111    | 3               | -20.6           |
| 34           | d.lin.t.34.3.111-111    | 3               | -14.8           |
| 37           | d.lin.c.37.3.111-111    | 3               | -12.0           |
| 44           | d.lin.t.44.3.111-111    | 3               | -7.5            |
| 47           | d.lin.c.47.3.111-111    | 3               | -1.5            |
| 77           | s.lin.t.77.2.011-011    | 2               | -5.2            |

ᵃEnergy relative to the lowest energy isomer with Ox3 (22, 23, 24, 27 and 77 connectivity) or Ox2 (33, 34, 37, 44, 47) oxidation state.

SI5. **Distribution plots for S₁-S₃ excitation energy and oscillator strength**

See Figure SI6 in the next page. Caption:

**Figure SI6.** Distribution of S₁-S₃ excitation energy (a-c, respectively) and oscillator strength (d-f) for the dimers grouped by oxidation state and resonance/bonding, separating linear from cyclic. The filled boxes cover the second and third quartile of each group, and the whiskers the full range from the lowest to the highest absorption. The label includes the number of compounds from each type. Color coding: Linear and cyclic compounds of the same resonance/bonding type are plotted with the same color, eg all linear s compounds in light blue and all cyclic s compounds in dark blue. The vertical dashed lines in (a) are, for reference, the absorption of the DHI monomer and the oxidized IQ, NQ and MQ monomers.
Excitation energy [eV]

Ox0.lin.s (20)
Ox1.lin.s (96)
Ox1.lin.d (56)
Ox1.lin.z (94)
Ox2.lin.s (156)
Ox2.lin.d (42)
Ox2.lin.z (54)
Ox3.lin.d (12)
Ox3.lin.z (8)
Ox0.cyc.s (18)
Ox1.cyc.s (64)
Ox1.cyc.d (29)
Ox1.cyc.z (75)
Ox2.cyc.s (64)
Ox2.cyc.d (20)
Ox2.cyc.z (18)
Ox3.cyc.d (4)

Oscillator strength

Ox0.lin.s (20)
Ox1.lin.s (96)
Ox1.lin.d (56)
Ox1.lin.z (94)
Ox2.lin.s (156)
Ox2.lin.d (42)
Ox2.lin.z (54)
Ox3.lin.d (12)
Ox3.lin.z (8)
Ox0.cyc.s (18)
Ox1.cyc.s (64)
Ox1.cyc.d (29)
Ox1.cyc.z (75)
Ox2.cyc.s (64)
Ox2.cyc.d (20)
Ox2.cyc.z (18)
Ox3.cyc.d (4)
SI6. **Construction of absorption/stability plots**
To construct the absorption/stability plots (Figure 5), for every group of compounds a two-dimensional grid of bins is created with a spacing of 0.125 eV (x axis) and 5 kcal·mol$^{-1}$ (y axis) (eg 41 x 5 for Figure 5a). The contents of every bin, $z_{ij}$, is the sum of the oscillator strengths assigned to that bin according to the following formula:

$$z_{ij} = \sum_{p,q} f_{pq} \left( G_p \in [G_j], E_{pq} \in [E_i] \right)$$  \hspace{1cm} [S3]

where the sum runs over $p$, the number of compounds in the group, and $q=1,3$, the number of vertical excitations calculated for every compound. The sum is performed when the energy of compound $p$, $G_p$, and the excitation energy $E_{pq}$ fall into the bin relative energy and excitation ranges ($G_j$ and $E_i$, respectively). After the sum is performed, the values of $z$ are normalized to 1 dividing by the maximum of $z_{ij}$.

SI7. **Analysis of absorptions contributing to highlighted signals in stability vs absorption plots**
For every highlighted signal of Figure 5, the compounds that contribute most to the absorption (largest oscillator strength) are listed in Tables SI3 and SI4 (linear and cyclic dimers, respectively). The structures are displayed in Schemes 2, 3 and SI3. Orbital plots are provided in Figure SI7.
## Table SI3. Most significant contributions to the highlighted absorption signals of the stability vs absorption plots, linear dimers (Figure 5a-d).

| Group | Signal | $G_{ev}$ [kcal·mol$^{-1}$] | $E_{exc}$ [eV] | $f$ | State | Compound name | Type | Scheme |
|-------|--------|-----------------|-------------|-----|-------|-----------------|------|--------|
| Ox0-lin A | 0.0 | 3.87 | 1.4002 | $S_1$ | s.lin.t.22.0.000-000 | Ox0-AA-s | 2 |
|       | 1.2 | 3.89 | 1.3618 | $S_1$ | s.lin.c.22.0.000-000 | Ox0-AA-s | SI3 |
| B     | 2.7 | 4.09 | 0.8725 | $S_1$ | s.lin.c.27.0.000-000 | Ox0-AB-s | 2 |
|       | 2.9 | 4.00 | 0.8724 | $S_1$ | s.lin.c.24.0.000-000 | Ox0-AB-s | SI3 |
|       | 3.6 | 4.09 | 0.8481 | $S_1$ | s.lin.t.24.0.000-000 | Ox0-AB-s | SI3 |
| C     | 1.1 | 4.26 | 0.8383 | $S_1$ | s.lin.c.23.0.000-000 | Ox0-AA-s | SI3 |
|       | 1.6 | 4.30 | 0.7923 | $S_1$ | s.lin.t.23.0.000-000 | Ox0-AA-s | SI3 |
|       | 3.3 | 4.28 | 0.7777 | $S_1$ | s.lin.t.27.0.000-000 | Ox0-AB-s | SI3 |
| D     | 3.8 | 4.71 | 0.4052 | $S_2$ | s.lin.t.37.0.000-000 | Ox0-AB-s | SI3 |
|       | 3.3 | 4.75 | 0.3787 | $S_3$ | s.lin.t.33.0.000-000 | Ox0-AA-s | SI3 |
|       | 4.1 | 4.71 | 0.3159 | $S_1$ | s.lin.c.33.0.000-000 | Ox0-AA-s | SI3 |
|       | 3.8 | 4.65 | 0.2735 | $S_1$ | s.lin.t.37.0.000-000 | Ox0-AB-s | SI3 |
|       | 3.8 | 4.71 | 0.2504 | $S_2$ | s.lin.t.37.0.000-000 | Ox0-AB-s | SI3 |
|       | 1.1 | 4.76 | 0.2414 | $S_1$ | s.lin.c.23.0.000-000 | Ox0-AA-s | SI3 |
| Ox1-lin E | 8.2 | 1.70 | 0.2704 | $S_1$ | z.lin.t.23.1.001-001 | Ox1-AA-z | 2 |
| F     | 0.0 | 2.32 | 1.7509 | $S_1$ | d.lin.c.22.1.001-001 | Ox1-AA-d | 2 |
| G     | 6.0 | 2.83 | 1.2455 | $S_2$ | s.lin.c.22.1.101-000 | Ox1-AA-s | SI3 |
|       | 8.1 | 2.81 | 1.1386 | $S_2$ | s.lin.t.22.1.101-000 | Ox1-AA-s | SI3 |
|       | 8.2 | 2.77 | 0.8346 | $S_1$ | z.lin.t.23.1.001-001 | Ox1-AA-z | SI3 |
|       | 5.9 | 2.85 | 0.8222 | $S_1$ | d.lin.t.24.1.001-010 | Ox1-AB-d | SI3 |
| H     | 4.4 | 2.88 | 1.1785 | $S_1$ | d.lin.c.23.1.001-100 | Ox1-AA-d | SI3 |
|       | 2.7 | 2.93 | 1.0876 | $S_1$ | s.lin.t.22.1.011-000 | Ox1-AA-s | SI3 |
|       | 4.4 | 2.95 | 1.0451 | $S_1$ | s.lin.t.22.1.011-000 | Ox1-AA-s | SI3 |
|       | 3.0 | 2.93 | 1.0347 | $S_1$ | d.lin.t.23.1.001-100 | Ox1-AA-d | SI3 |
|       | 3.2 | 2.80 | 0.8264 | $S_1$ | d.lin.c.24.1.001-010 | Ox1-AB-d | SI3 |
| Ox2-lin I | 4.6 | 1.87 | 0.1505 | $S_1$ | s.lin.t.22.2.011-011 | Ox2-AA-s | SI3 |
|       | 3.9 | 1.75 | 0.1401 | $S_1$ | s.lin.c.27.2.011-011 | Ox2-AB-s | 2 |
|       | 4.0 | 1.82 | 0.1267 | $S_1$ | s.lin.t.23.2.011-011 | Ox2-AA-s | SI3 |
| J     | 10.2 | 1.78 | 0.2333 | $S_1$ | s.lin.t.23.2.011-101 | Ox2-AA-s | SI3 |
|       | 5.9 | 1.64 | 0.2046 | $S_1$ | s.lin.t.24.2.011-011 | Ox2-AB-s | SI3 |
|       | 6.4 | 1.80 | 0.1776 | $S_1$ | s.lin.t.27.2.011-011 | Ox2-AB-s | SI3 |
|       | 9.9 | 1.73 | 0.1735 | $S_1$ | s.lin.t.24.2.101-011 | Ox2-AB-s | SI3 |
| K     | 2.6 | 2.25 | 0.1723 | $S_1$ | d.lin.t.27.2.001-111 | Ox2-AB-d | 2 |
| L     | 2.7 | 2.73 | 0.9111 | $S_3$ | d.lin.c.24.2.001-111 | Ox2-AB-d | SI3 |
|       | 4.2 | 2.73 | 0.8692 | $S_3$ | d.lin.t.27.2.001-111 | Ox2-AB-d | SI3 |
|       | 4.7 | 2.78 | 0.9011 | $S_3$ | d.lin.t.24.2.001-111 | Ox2-AB-d | SI3 |
| Ox3-lin M | 9.2 | 2.65 | 0.2221 | $S_2$ | d.lin.t.37.3.111-111 | Ox3-AB-d | SI3 |
|       | 9.3 | 2.62 | 0.1924 | $S_2$ | d.lin.c.37.3.111-111 | Ox3-AB-d | SI3 |
**Table SI4.** Most significant contributions to the highlighted absorption signals of the stability vs absorption plots, cyclic dimers (Figure 5e-h).

| Group  | Signal | $G_{rel}$ [kcal·mol$^{-1}$] | $E_{exc}$ [eV] | $f$ | State | Compound name | Type | Scheme |
|--------|--------|-----------------------------|---------------|-----|-------|---------------|------|--------|
| Ox0-cyc | N      | 1.8                         | 3.38          | 0.3404 | $S_1$  | s.cyc.34.34.0.000-000 | Ox0-6C6-s | SI4 |
|        | P      | 0.0                         | 3.76          | 0.5672 | $S_1$  | s.cyc.34.43.0.000-000 | Ox0-6C6-s | 3    |
| Ox1-cyc | Q      | 1.3                         | 1.37          | 0.1701 | $S_1$  | z.cyc.34.43.1.010-010 | Ox1-6C6-z | 3    |
|        |        | 3.8                         | 1.31          | 0.1064 | $S_1$  | s.cyc.34.43.1.000-011 | Ox1-6C6-s | SI4 |
|        |        | 8.6                         | 1.24          | 0.0889 | $S_1$  | z.cyc.34.43.1.001-010 | Ox1-6C6-z | SI4 |
|        |        | 9.7                         | 1.27          | 0.0874 | $S_1$  | s.cyc.34.43.1.000-110 | Ox1-6C6-s | SI4 |
|        |        | 4.5                         | 1.13          | 0.081  | $S_1$  | s.cyc.34.43.1.011-000 | Ox1-6C6-s | SI4 |
|        | R      | 0.7                         | 1.90          | 0.1198 | $S_1$  | d.cyc.34.43.1.010-100 | Ox1-6C6-d | 3    |
|        |        | 2.8                         | 1.76          | 0.0924 | $S_2$  | d.cyc.34.43.1.010-010 | Ox1-6C6-d | SI4 |
|        |        | 0.0                         | 1.79          | 0.0897 | $S_1$  | s.cyc.34.43.1.110-000 | Ox1-6C6-s | 3    |
| Ox2-cyc | S      | 9.1                         | 1.31          | 0.1900 | $S_1$  | s.cyc.34.43.2.011-011 | Ox2-6C6-s | 3    |
| Ox3-cyc | T      | 0.0                         | 3.30          | 0.0973 | $S_1$  | d.cyc.34.43.3.111-111 | Ox3-6C6-d | 3    |
Scheme SI3. Additional compounds highlighted in Figure 5 (linear dimers). Labelling follows the convention of Scheme 2 and 3 in the main text.
Scheme SI4. Additional compounds highlighted in Figure 5 (cyclic dimers). Labelling follows the convention of Schemes 2 and 3 in the main text.
Figure SI7. Orbital plots with the main contribution to the absorptions corresponding to signals A-E in Figure 5.
Figure SI8. Orbital plots with the main contribution to the absorptions corresponding to signals F-I in Figure 5.
Figure SI9. Orbital plots with the main contribution to the absorptions corresponding to signals J-M in Figure 5.
Figure SI10. Orbital plots with the main contribution to the absorptions corresponding to signals N-T in Figure 5.
SI References

[1] a) A. D. Laurent, D. Jacquemin, *Int. J. Quantum Chem.* 2013, **113**, 2019-2039; b) C. Suellen, R. G. Freitas, P.-F. Loos, D. Jacquemin, *J. Chem. Theory Comput.* 2019, **15**, 4581-4590.

[2] A. Dreuw, M. Head-Gordon, *Chem. Rev.* 2005, **105**, 4009-4037.

[3] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378-6396.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Rudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, 2016.

[5] P. Ghosh, D. Ghosh, *J. Phys. Chem. B* 2017, **121**, 5988-5994.

[6] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**.

[7] D. Ghosh, *WIREs Comput. Mol. Sci.* 2021, **11**.

[8] M. Mammen, E. I. Shakhnovich, J. M. Deutch, G. M. Whitesides, *J. Org. Chem.* 1998, **63**, 3821-3830.

[9] M. N. Kutty, *Vol. 2021*, 1987.

[10] M. d'Ischia, K. Wakamatsu, A. Napolitano, S. Briganti, J.-C. Garcia-Borron, D. Kovacs, P. Meredith, A. Pezzella, M. Picardo, T. Sarna, J. D. Simon, S. Ito, *Pigment Cell Melanoma Res.* 2013, **26**, 616-633.