Supporting information for the article

Deciphering the broadband absorption of eumelanin in solution phase

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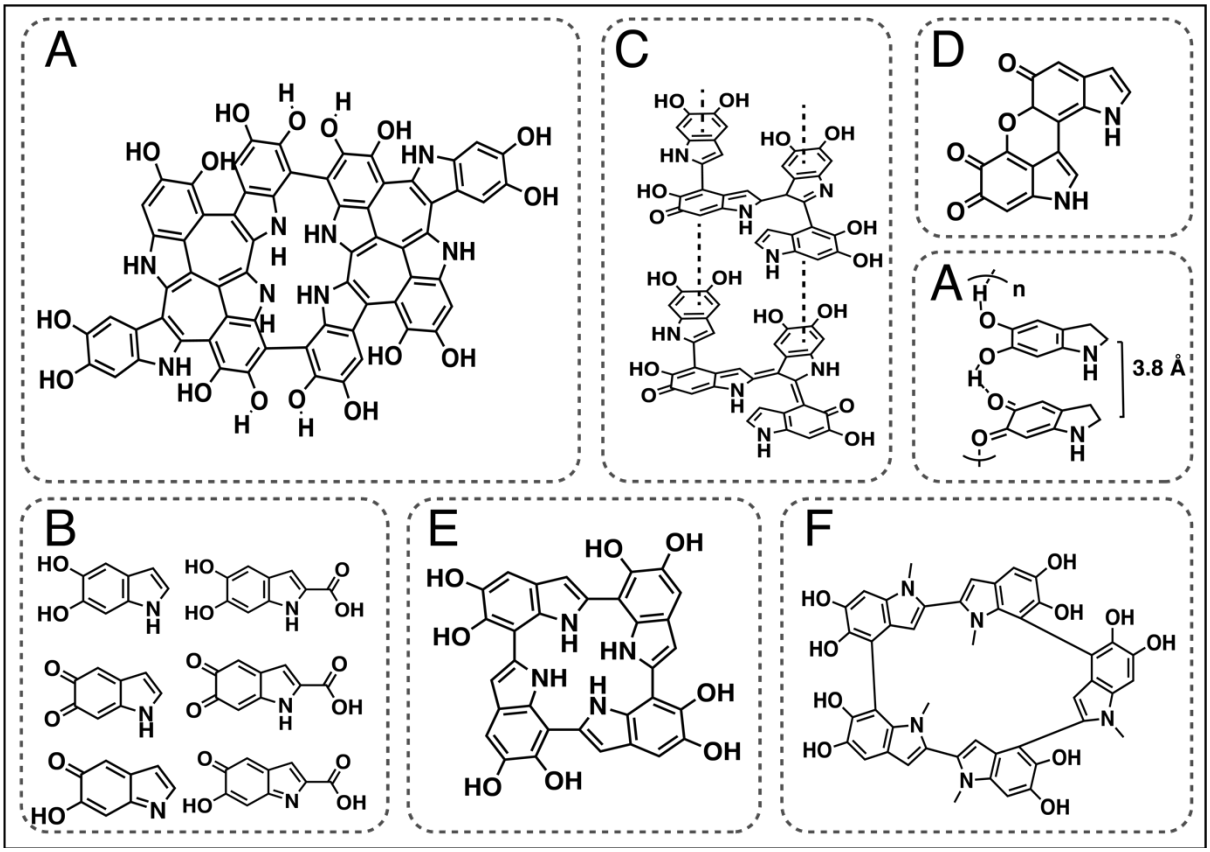


Figure S1: Proposed structural models of eumelanin: **(A)** Hexameric and octameric fused structural models, **(B,E)** π-stacked and H-bonded build-up of redox states of DHI and DHICA, **(C)** Linear covalent tetrameric structural model, **(F)** Porphyrin ring like structure model and **(G)** Macrocyclic structure arising from oligomer-oligomer coupling.

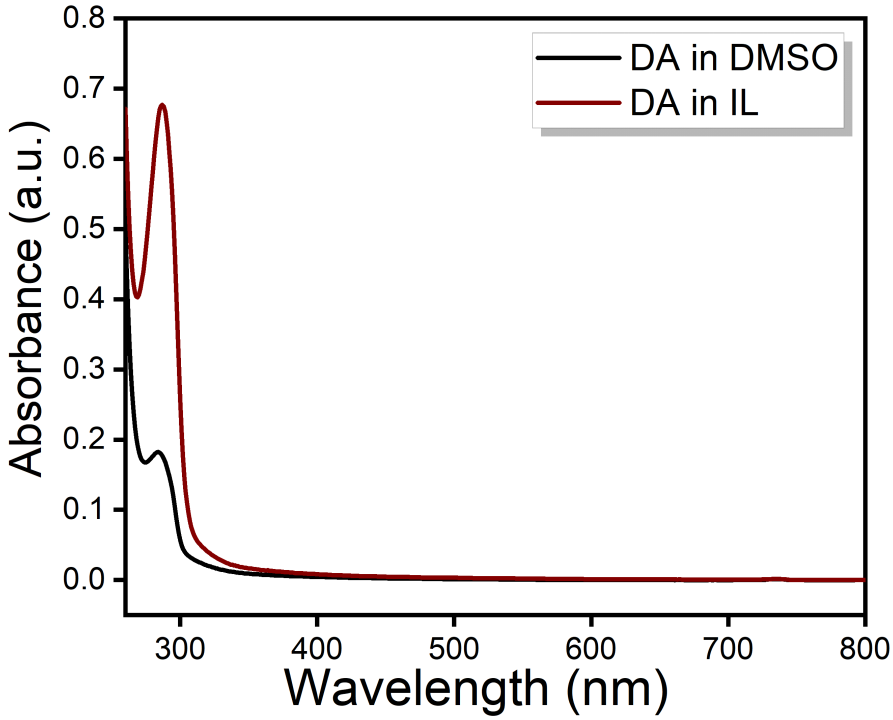


Figure S2: UV-Vis absorption spectra of DA recorded in [C_2mim][OAc] (red line) and DMSO (black line).

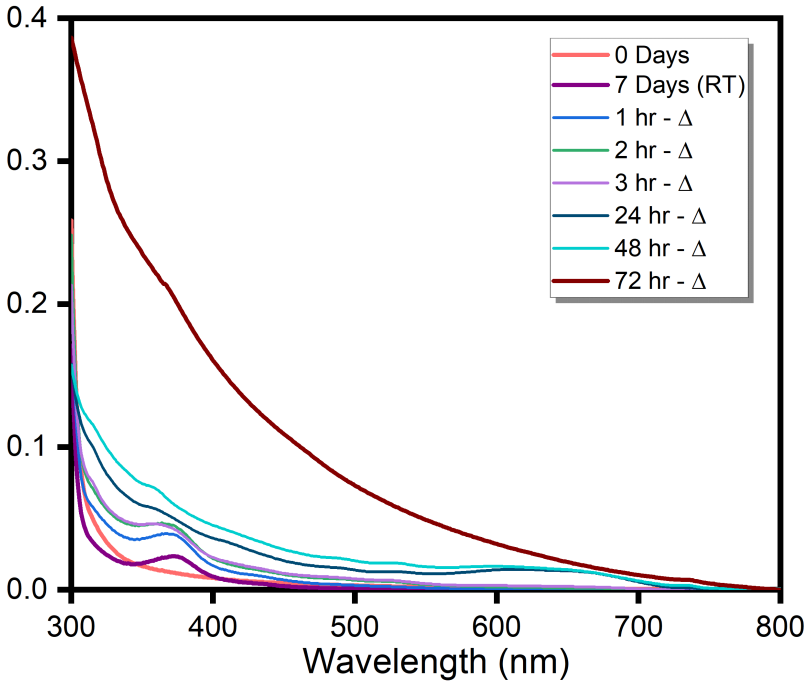


Figure S3: Evolution of absorption spectra of DA polymerised in [C_2mim][OAc], heating time indicates the heating of solution at 80 °C after 7 days.

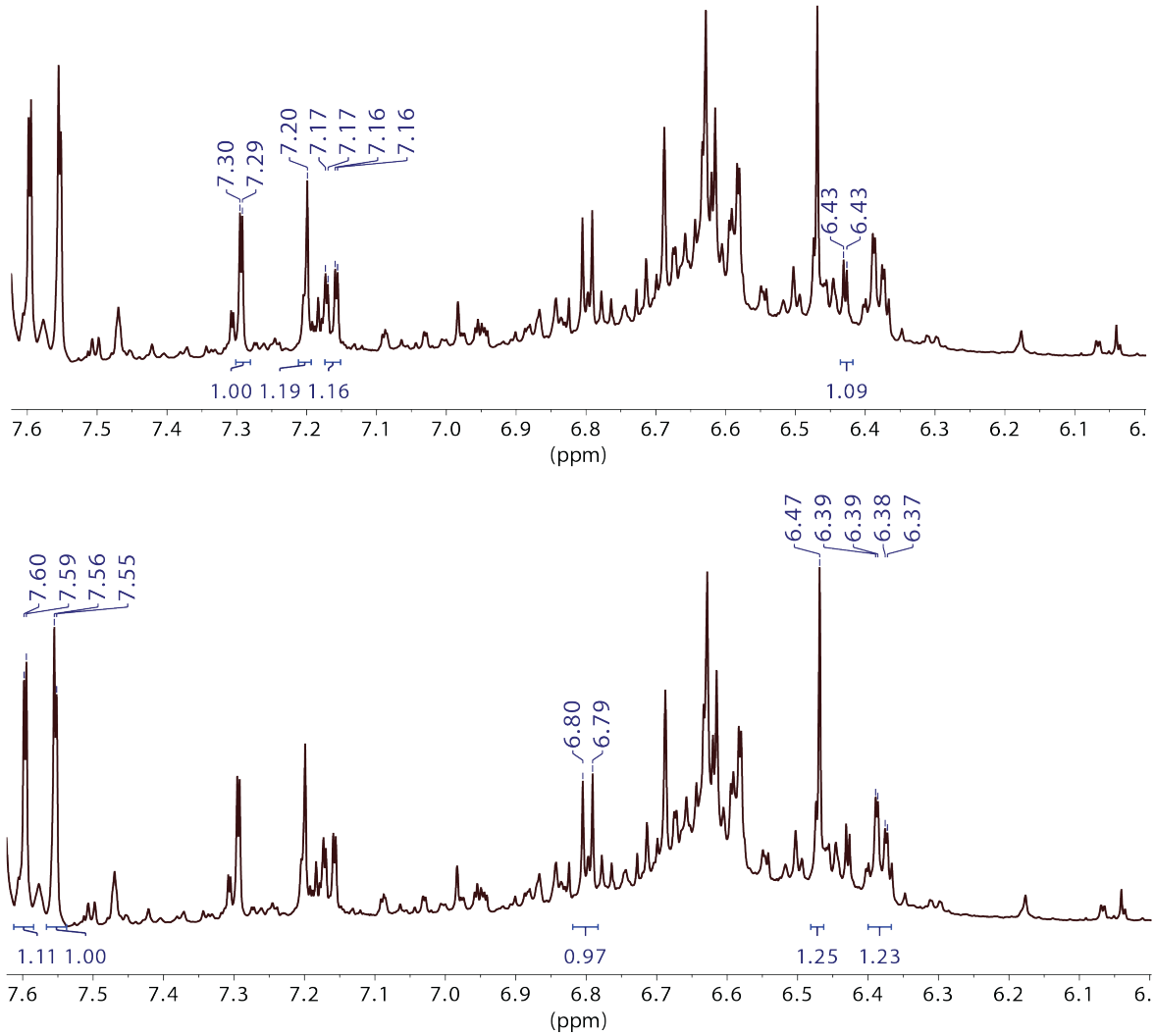


Figure S4: ^{1}H-NMR analysis of DA polymerized in [C_2mim][OAc] after complete polymerization. The spectrum was recorded in DMSO-d_6. The aromatic region of the spectrum is shown in two sets for clarity.

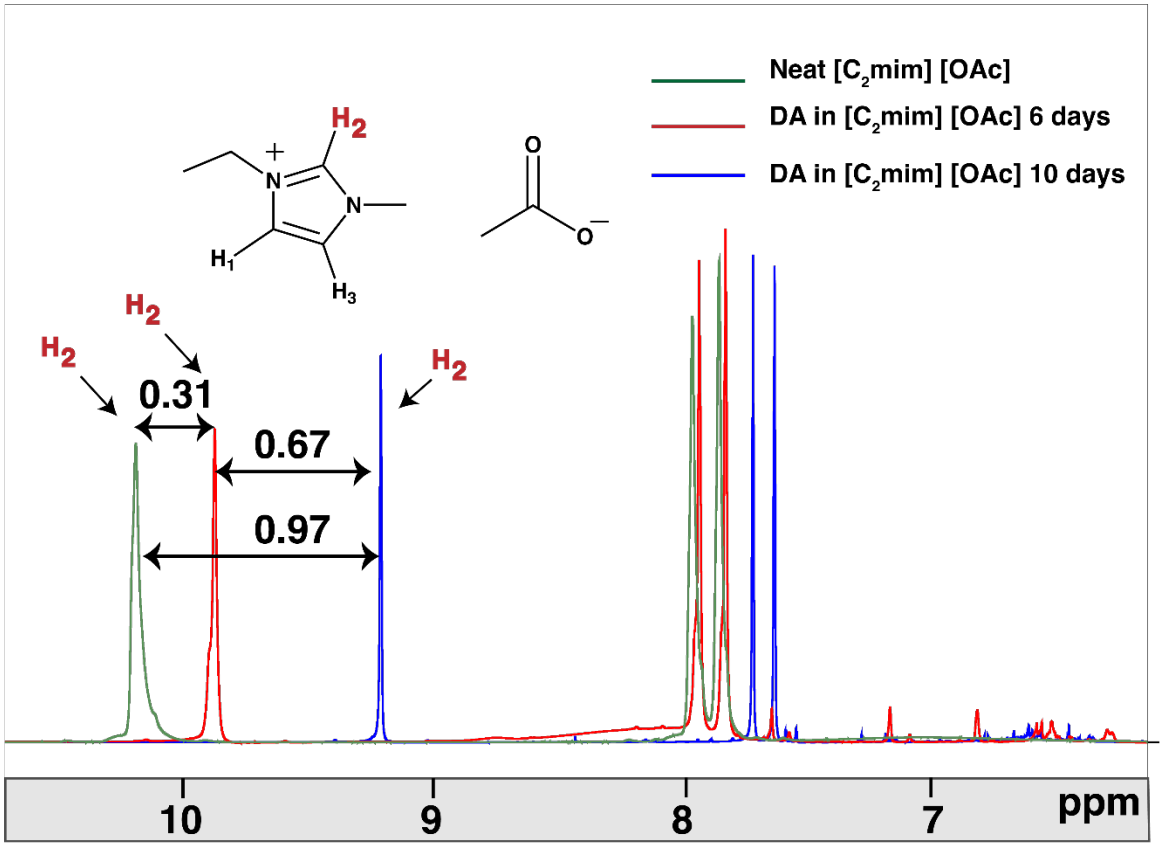


Figure S5: ^{1}H-NMR spectrum of [C_2mim][OAc] (green lines) and the DA polymer solution in [C_2mim][OAc] after 6 days of polymerisation (red lines) and 10 days (blue lines). All spectra were recorded in DMSO-d6.

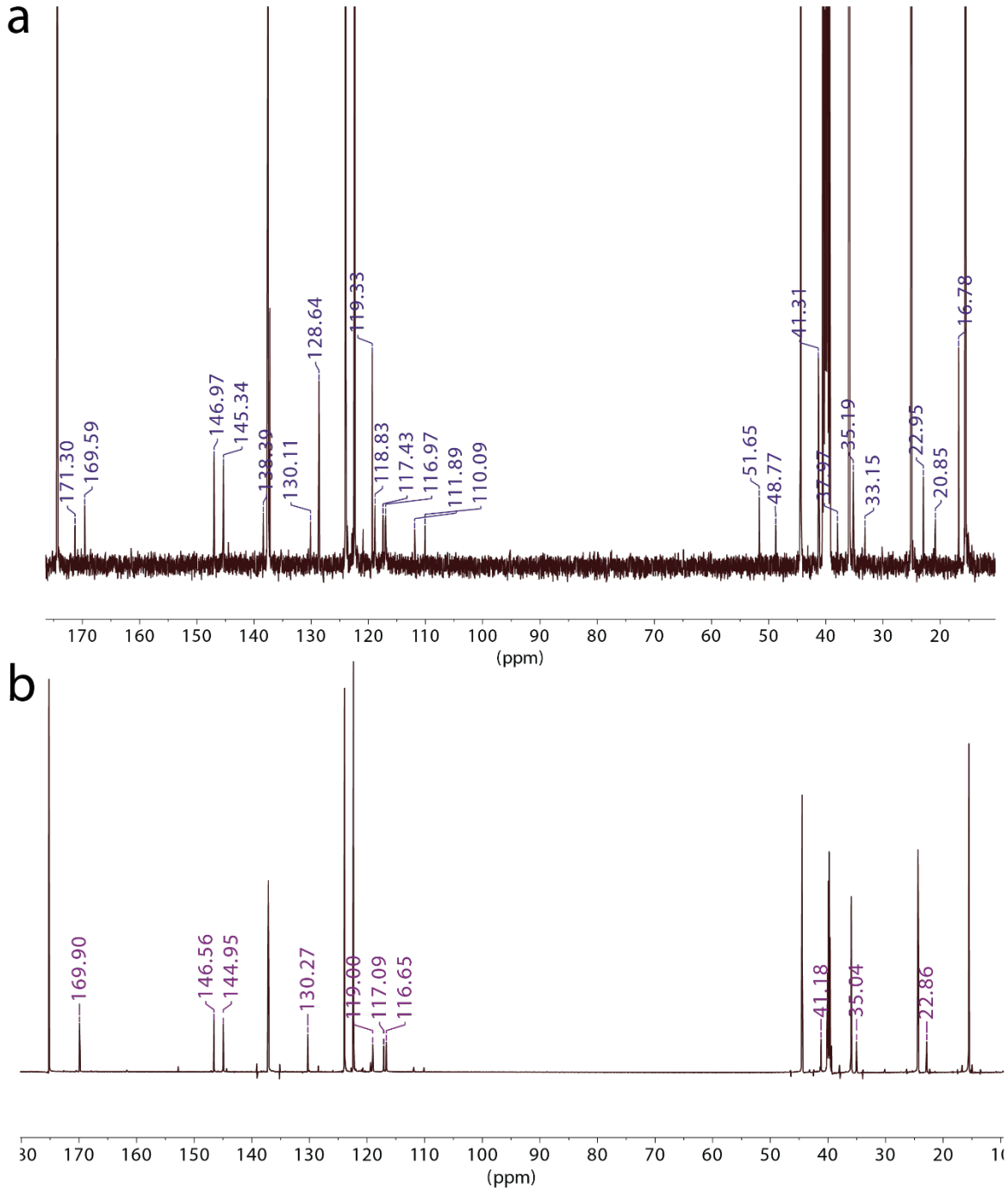


Figure S6*:* ^{13}C NMR analysis of DA polymerised in [C_2mim][OAc] after **a)** complete polymerization, 10 days, and after **b)** 6 days of the reaction time showing. All spectra were recorded in DMSO-d_6.

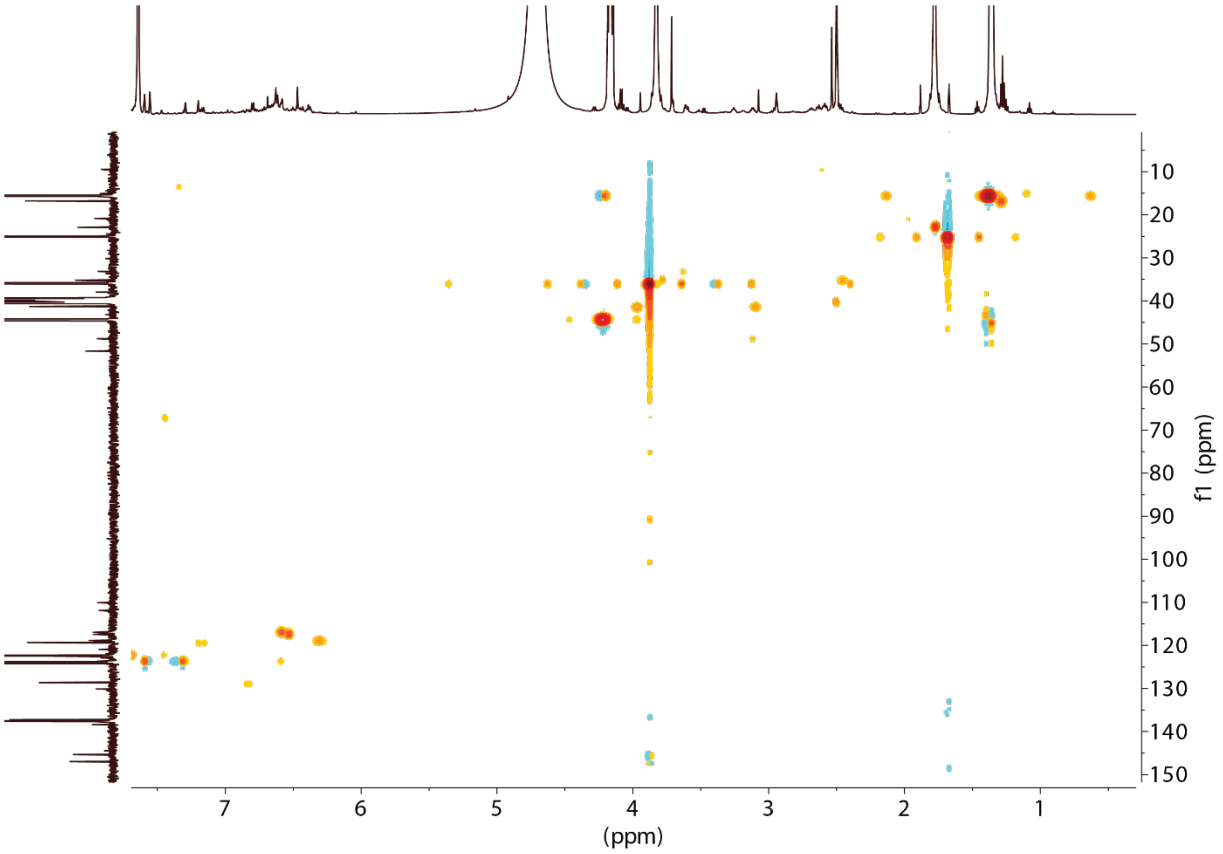
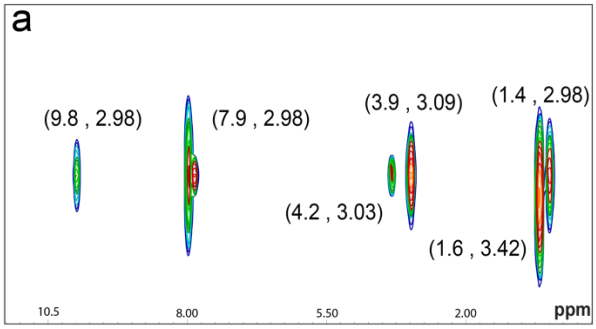


Figure S7: ^{1}H-^{13}C correlated chemical shifts (HSQC NMR) for DA polymerised in [C_2mim][OAc] after 10 days of the reaction time, (horizontal axis represents ^{1}H and vertical axis represents ^{13}C).

Table S1: One-to-one correlation of ^{13}C to ^{1}H signals and possible polymerization products responsible for those signals.

F2 (ppm)	F1 (ppm)	Annotation	F2 (ppm)	F1 (ppm)	Annotation
7.68	122.4	Dimer	3.64	35.9	Cyclic monomer/dimer
7.58	123.9	Dimer	3.63	33.2	Cyclic monomer/dimer
7.20	119.4	Dimer	3.48	37.9	Cyclic monomer/dimer
6.84	128.8	Dimer	3.38	35.9	Cyclic monomer/dimer
6.59	123.7	Monomer	3.11	48.8	Cyclic monomer/dimer
6.58	116.9	Monomer	3.09	41.2	Cyclic monomer/dimer
6.53	117.4	Monomer	2.71	42.4	Cyclic monomer/dimer
6.50	110.1	Monomer	2.65	35.9	Cyclic monomer/dimer

a



b

^{1}H-NMR (ppm)	Diffusion Coefficient (m^2/s)	Radius (Å)
9.8	2.98×10^{-10}	3.66
7.9	2.98×10^{-10}	3.66
4.2	3.03×10^{-10}	3.60
3.9	3.09×10^{-10}	3.53
1.6	3.42×10^{-10}	3.19
1.4	2.98×10^{-10}	3.66

c

^{1}H-NMR (ppm)	Diffusion Coefficient (X 10^{-10} m^2/s)	Radius (Å)	% Occurrence
6.80	1.15	9.49	3.06
6.40	0.60	18.18	5.33
6.20	0.87	12.54	8.26
6.00	0.80	13.64	2.48
5.70	0.65	16.78	3.03
5.70	1.43	7.63	4.16
2.30	1.43	7.63	9.66
1.80	1.43	7.63	8.77
3.10	2.34	4.66	20.99
7.10	2.07	5.27	29.85
7.00	2.34	4.66	4.41

Figure S8. **a)** Diffusion coefficients for the peaks obtained from [C_2mim][OAc] in a mixture of polymerized DA solution. Analysis for [C_2mim][OAc] peaks yield diffusion coefficients of ~ 3×10^{-10} m^2/s. Values next to the signals represent (^{1}H signal in ppm, diffusion coefficient). **b)** Calculated radii for each peak obtained for DOSY spectra. This can be concluded that in a mixture of signals different signals corresponding to one structure yield similar diffusion coefficients. **c)** Calculated radii from the diffusion coefficients of DOSY peaks obtained from the polymerized DA (Fig. 3b, main text). Further integration of the peaks yielded relative percentage occurrence of the molecules of various sizes in the polymer solution.

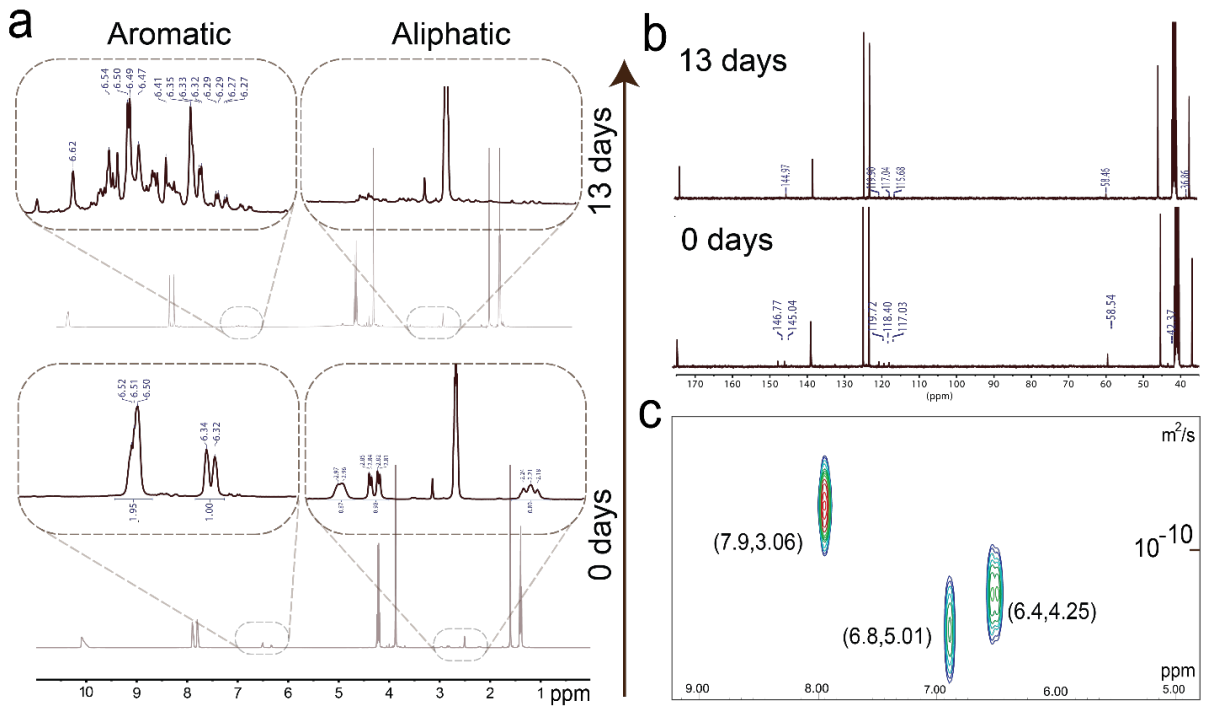


Figure S9. Structural evolution of L-DOPA polymerized in [C_2mim][OAc], a) ^{1}H-NMR of polymerized L-DOPA at the beginning of the reaction (0 days) and after the polymerization (13 days). All aromatic and aliphatic signals arising from L-DOPA has been zoomed out and signals. After the complete polymerization aliphatic signals disappear and aromatic signals show a scattered signal. However, the spread of signals in polymerized L-DOPA is much less in comparison to the DA. b) ^{13}C-NMR of polymerized L-DOPA at the beginning of the reaction (0 days) and after the polymerization (13 days). Unlike DA there are no indications of stable redox species (C=O, peaks) in L-DOPA. c) DOSY measurements yielded only three signals in polymerized L-DOPA with diffusion coefficients corresponding to the sizes of 1.70 Å, 2.18 Å and 3.57 Å, indicating the presence of homogeneous short molecules (no longer than monomers) in the final solution. Values next to the signals represent (^{1}H signal in ppm, diffusion coefficient). All spectra were recorded in DMSO-d_6.

Computational procedures:

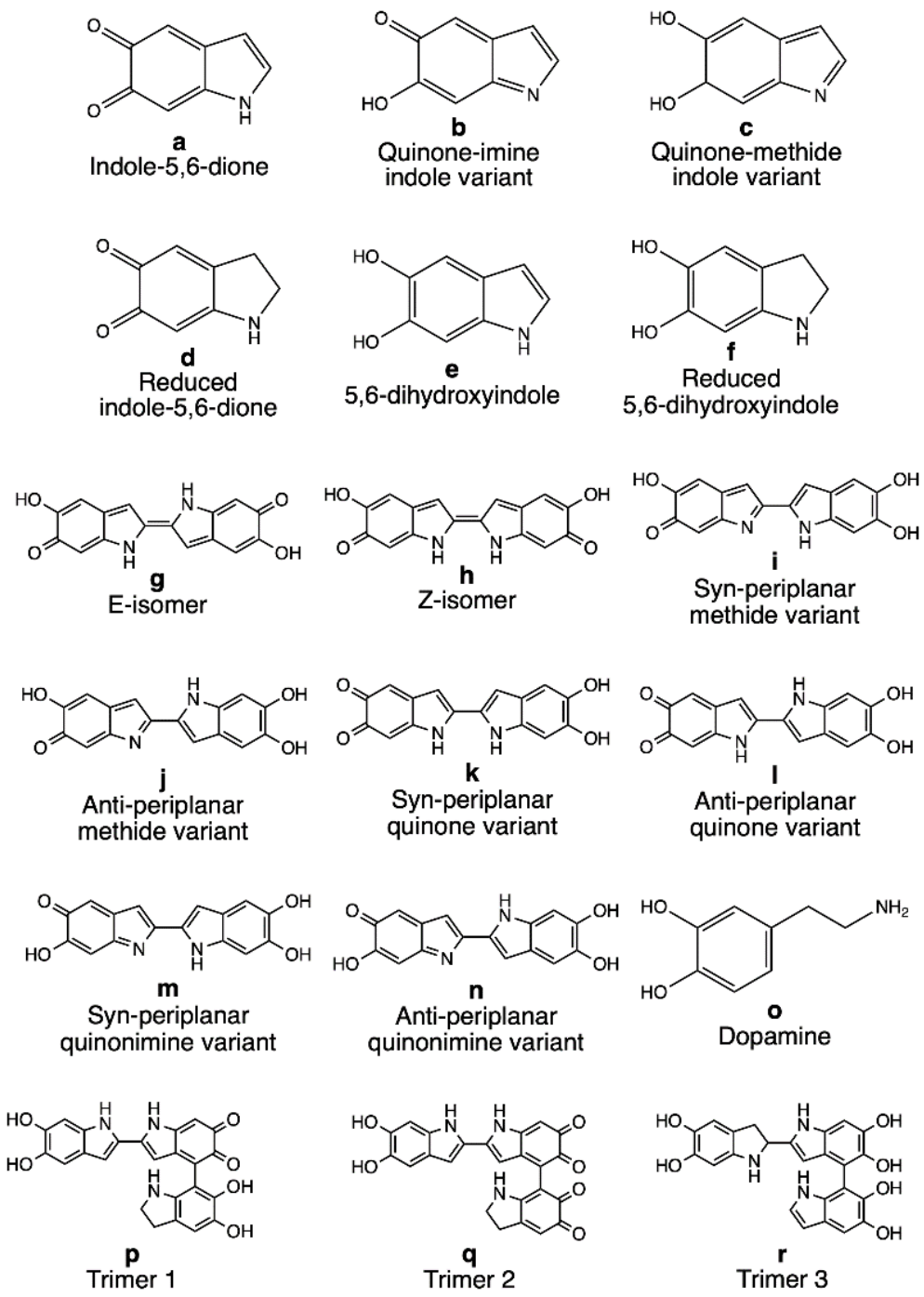


Figure S10: Chemical species considered in the computational chemistry study.

UV-Visible spectra predicted by Orca:

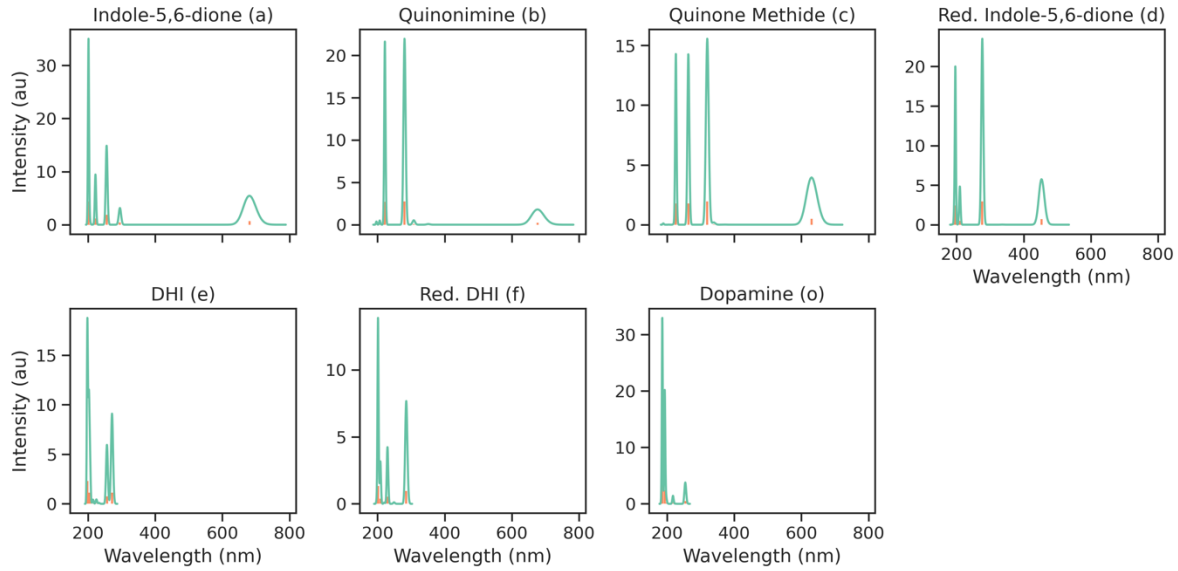


Figure S11: Predicted UV-Visible spectra of individual monomers. The *x*-axis shows wavelengths in nm and the *y*-axis shows absorption intensity in arbitrary units.

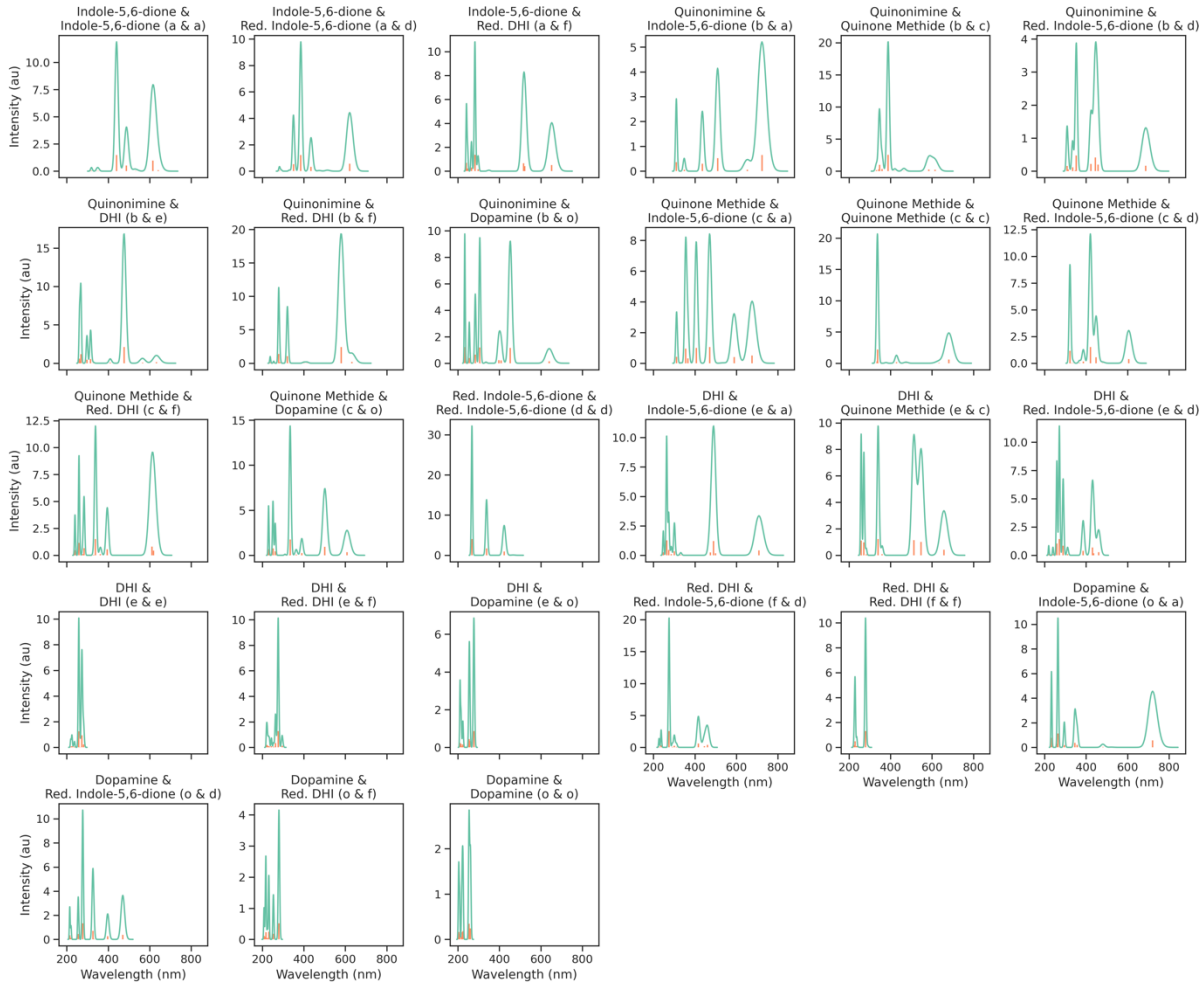


Figure S12: *Predicted UV-Visible spectra of stacked monomers.* The x-axis shows wavelengths in nanometers and the y-axis shows absorption intensity in arbitrary units.

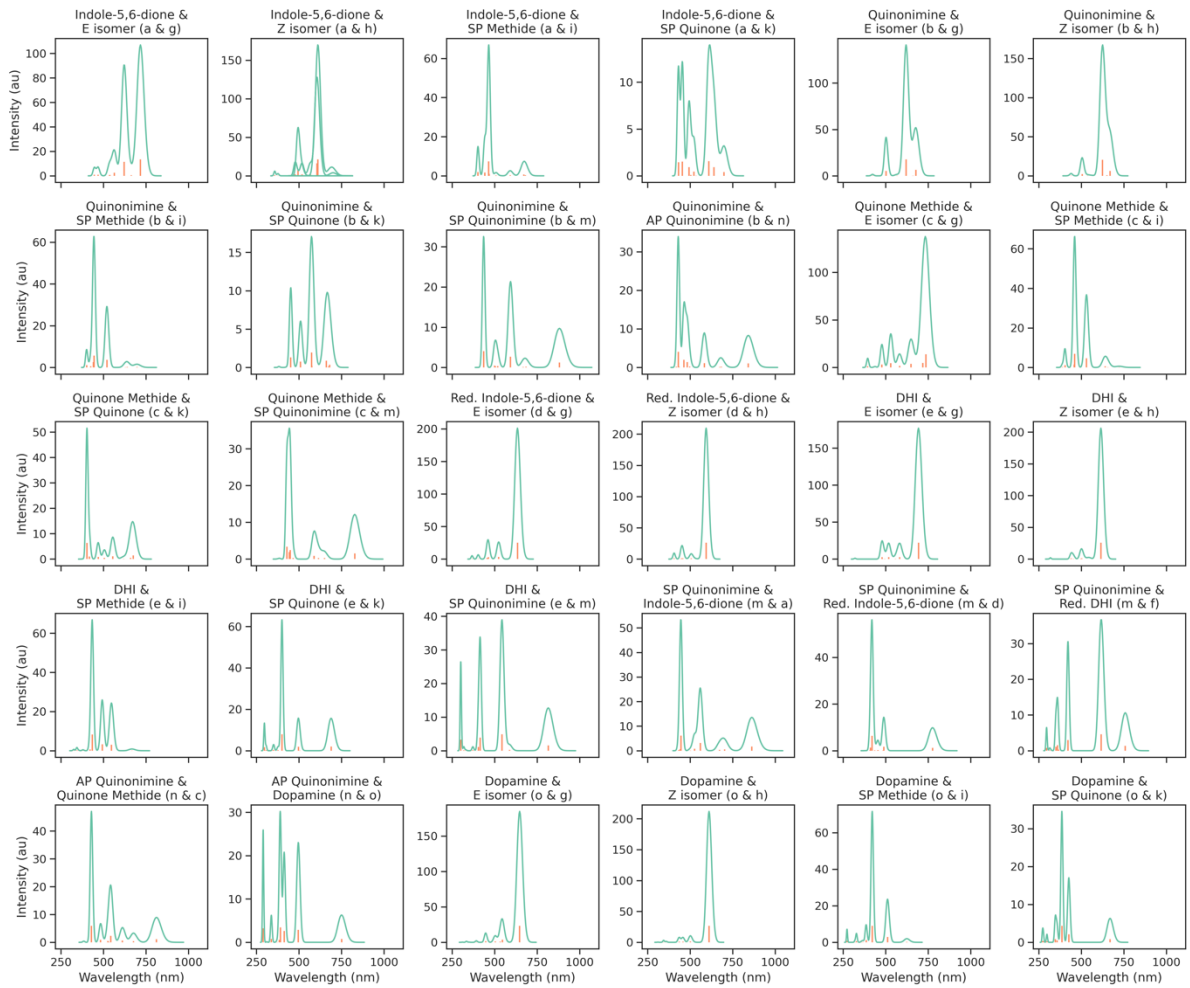


Figure S13*:* Predicted UV-Visible spectra of stacked monomers and covalent dimers. Here two monomers were combined with one covalent dimer. The x-axis shows wavelengths in nanometers and the y-axis shows absorption intensity in arbitrary units.

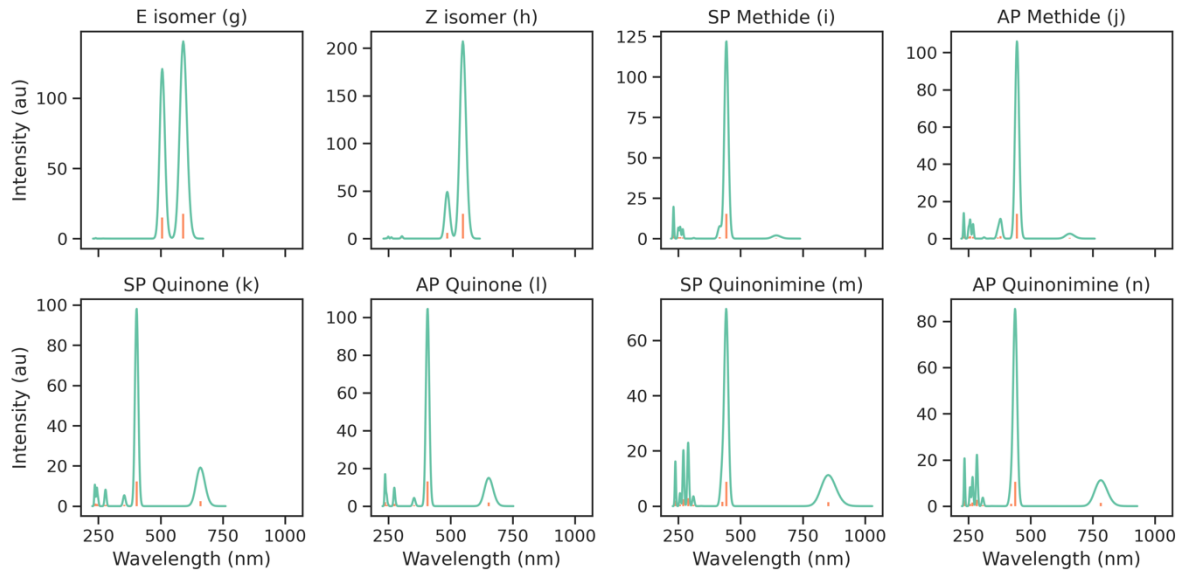


Figure S14: *Predicted UV-Visible spectra of individual covalent dimers.* The x-axis shows wavelengths in nanometers and the y-axis shows absorption intensity in arbitrary units.

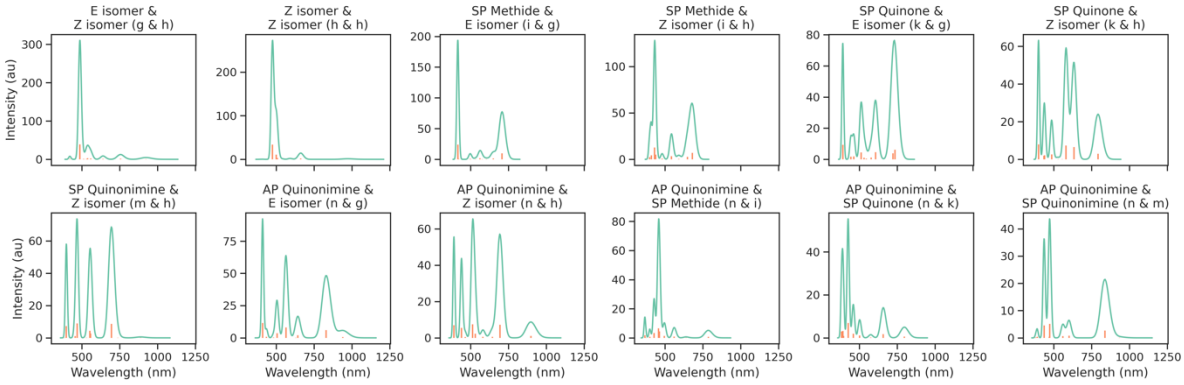


Figure S15*: Predicted UV-Visible spectra of stacked dimers.* The *x*-axis shows wavelengths in nm and the *y*-axis shows absorption intensity in arbitrary units.

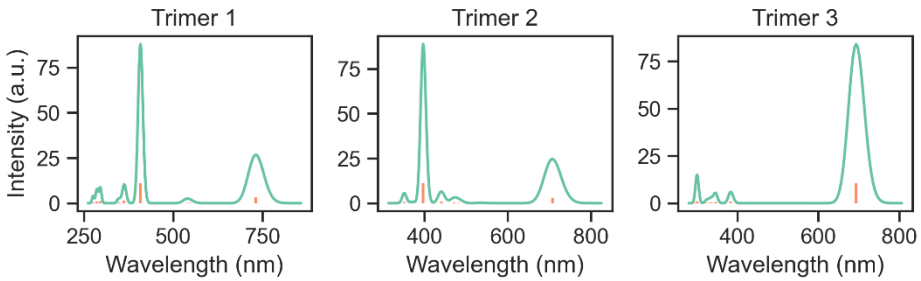


Figure S16*: Predicted UV-Visible spectra of covalent trimers.* The x-axis shows wavelengths in nm and the y-axis shows absorption intensity in arbitrary units.

Table S2: Tabulated data, showing the wavelength and its intensity of the maximum intensity peak each chemical structure and stacked complex. The intensities given are the gaussian-fitted values.

Structure Type	Molecules Involved	Wavelength (nm)	Intensity (au)
Individual Monomers	Dopamine	186	$7.91\text{x}10^{-1}$
	DHI	198	$4.50\text{x}10^{-1}$
	Indole-5,6-dione	201	$8.65\text{x}10^{-1}$
	Red. DHI	201	$2.59\text{x}10^{-1}$
	Red. Indole-5,6-dione	276	$5.79\text{x}10^{-1}$
	Quinonimine	280	$5.45\text{x}10^{-1}$
	Quinone Methide	319	$3.78\text{x}10^{-1}$
Stacked Monomers	Quinonimine & Dopamine	233	$2.39\text{x}10^{-1}$
	Dopamine & Dopamine	254	$6.60\text{x}10^{-2}$
	DHI & DHI	258	$2.44\text{x}10^{-1}$
	DHI & Indole-5,6-dione	263	$2.49\text{x}10^{-1}$
	Dopamine & Indole-5,6-dione	264	$2.16\text{x}10^{-1}$
	Red. Indole-5,6-dione & Red. Indole-5,6-dione	267	$7.90\text{x}10^{-1}$
	DHI & Red. Indole-5,6-dione	271	$2.80\text{x}10^{-1}$
	Red. DHI & Red. Indole-5,6-dione	275	$4.97\text{x}10^{-1}$
	DHI & Red. DHI	276	$2.51\text{x}10^{-1}$
	Dopamine & Red. Indole-5,6-dione	277	$2.58\text{x}10^{-1}$
	DHI & Dopamine	277	$1.68\text{x}10^{-1}$
	Red. DHI & Red. DHI	279	$2.56\text{x}10^{-1}$
	Dopamine & Red. DHI	280	$1.01\text{x}10^{-1}$
	Indole-5,6-dione & Red. DHI	282	$2.65\text{x}10^{-1}$
	Quinone Methide & Dopamine	334	$3.38\text{x}10^{-1}$
	Quinone Methide & Quinone Methide	337	$4.28\text{x}10^{-1}$
	Quinone Methide & Red. DHI	338	$2.96\text{x}10^{-1}$
	DHI & Quinone Methide	340	$2.42\text{x}10^{-1}$
	Quinonimine & Red. Indole-5,6-dione	352	$9.04\text{x}10^{-2}$
	Indole-5,6-dione & Red. Indole-5,6-dione	385	$2.42\text{x}10^{-1}$
	Quinonimine & Quinone Methide	388	$5.00\text{x}10^{-1}$
	Quinone Methide & Red. Indole-5,6-dione	420	$2.96\text{x}10^{-1}$
	Indole-5,6-dione & Indole-5,6-dione	439	$2.85\text{x}10^{-1}$
	Quinone Methide & Indole-5,6-dione	470	$2.05\text{x}10^{-1}$
	Quinonimine & DHI	476	$4.10\text{x}10^{-1}$
	Quinonimine & Red. DHI	579	$4.66\text{x}10^{-1}$
	Quinonimine & Indole-5,6-dione	723	$1.27\text{x}10^{-1}$
Stacked Monomers and Dimers	Dopamine & SP Quinone	386	$8.39\text{x}10^{-1}$
	AP Quinonimine & Dopamine	390	$6.70\text{x}10^{-1}$
	DHI & SP Quinone	399	$1.56\text{x}10^{0}$
	Quinone Methide & SP Quinone	402	$1.23\text{x}10^{0}$

	SP Quinonimine & Red. Indole-5,6-dione	419	$1.26x10^{0}$
	Dopamine & SP Methide	420	$1.75x10^{0}$
	AP Quinonimine & Quinone Methide	429	$1.16x10^{0}$
	Quinone Methide & SP Quinonimine	429	$6.49x10^{-1}$
	Quinonimine & AP Quinonimine	430	$7.96x10^{-1}$
	DHI & SP Methide	433	$1.57x10^{0}$
	Quinonimine & SP Quinonimine	436	$7.74x10^{-1}$
	Quinonimine & SP Methide	445	$1.12x10^{0}$
	SP Quinonimine & Indole-5,6-dione	446	$1.19x10^{0}$
	Quinone Methide & SP Methide	461	$1.36x10^{0}$
	Indole-5,6-dione & SP Methide	465	$1.45x10^{0}$
	DHI & SP Quinonimine	543	$9.63x10^{-1}$
	Quinonimine & SP Quinone	573	$3.80x10^{-1}$
	Red. Indole-5,6-dione & Z isomer	594	$5.08x10^{0}$
	Indole-5,6-dione & Z isomer	598	$4.23x10^{0}$
	Indole-5,6-dione & SP Quinone	610	$3.07x10^{-1}$
	Dopamine & Z isomer	611	$5.22x10^{0}$
	DHI & Z isomer	615	$5.09x10^{0}$
	SP Quinonimine & Red. DHI	617	$9.01x10^{-1}$
	Quinonimine & E isomer	619	$3.45x10^{0}$
	Quinonimine & Z isomer	624	$4.02x10^{0}$
	Red. Indole-5,6-dione & E isomer	634	$4.95x10^{0}$
	Dopamine & E isomer	647	$4.57x10^{0}$
	DHI & E isomer	692	$4.29x10^{0}$
	Indole-5,6-dione & E isomer	717	$2.63x10^{0}$
	Quinone Methide & E isomer	737	$2.69x10^{0}$
Covalent Dimers	SP quinone	399	$2.42x10^{0}$
	AP Quinone	407	$2.59x10^{0}$
	AP Quinonimine	437	$2.05x10^{0}$
	SP quinonimine	437	$1.73x10^{0}$
	SP methide	438	$2.98x10^{0}$
	AP methide	440	$2.58x10^{0}$
	Z isomer	549	$5.12x10^{0}$
	E isomer	591	$3.41x10^{0}$
Stacked Covalent Dimers	SP Quinone & E isomer	389	$1.79x10^{0}$
	SP Quinone & Z isomer	398	$1.52x10^{0}$
	AP Quinonimine & E isomer	409	$2.28x10^{0}$
	SP Methide & E isomer	414	$4.55x10^{0}$
	AP Quinonimine & SP Quinone	425	$1.36x10^{0}$
	SP Methide & Z isomer	430	$2.44x10^{0}$
	AP Quinonimine & SP Methide	456	$1.28x10^{0}$
	SP Quinonimine & Z isomer	468	$1.74x10^{0}$
	AP Quinonimine & SP Quinonimine	472	$1.01x10^{0}$
	Z isomer & Z isomer	474	$6.54x10^{0}$
	E isomer & Z isomer	486	$7.66x10^{0}$
	AP Quinonimine & Z isomer	513	$1.45x10^{0}$
Covalent Trimers	Trimer 1	604	$3.26x10^{0}$
	Trimer 2	397	$2.20x10^{0}$
	Trimer 3	693	$2.07x10^{0}$

Influence of Basis set on UV-Vis absorption:

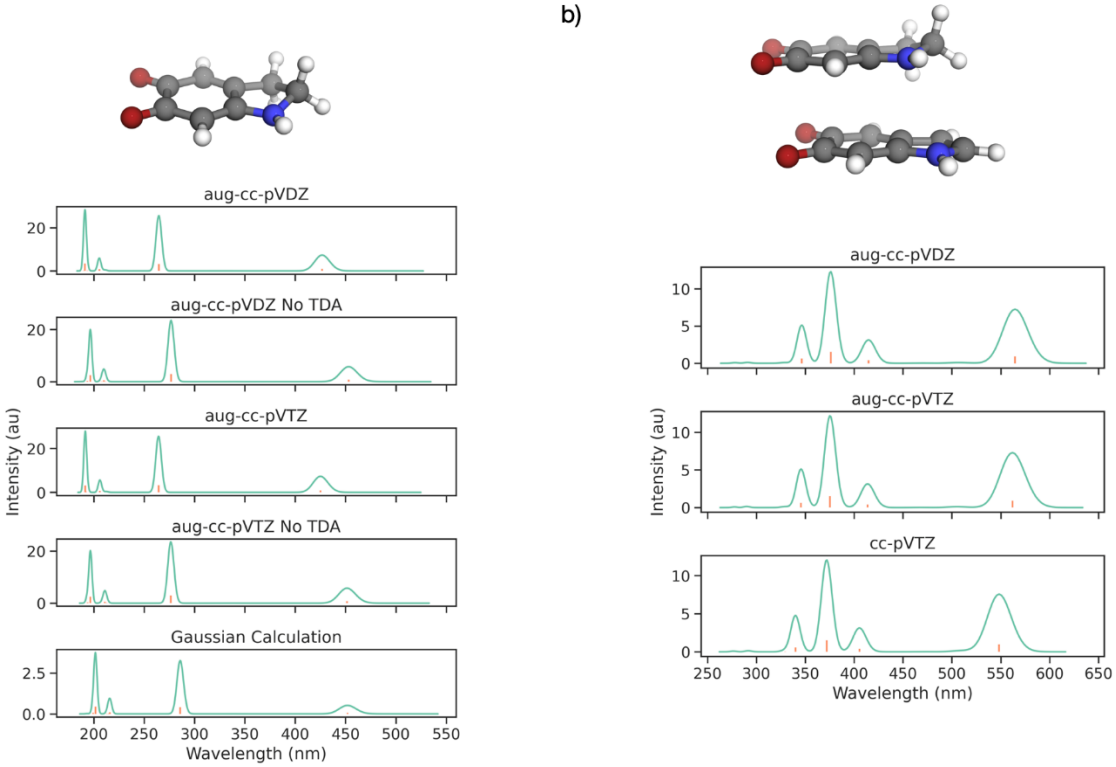


Figure S17: Influence of basis sets on the UV-Visible spectra of **a)** a reduced indole-5,6-dione molecule and **b)** a stacked configuration of indole-5,6-dione and reduced indole-5,6-dione molecules, performed with TD-DFT/ωB97XD. Note that the Gaussian16 calculation in **a)** was performed with an aug-cc-pVTZ basis set. The orange lines show the predicted wavelengths and intensities, while the green lines show the result of applying gaussian fitting to the predicted peaks. By default, TDA is applied to TD-DFT calculations in Orca as its inclusion is known to resolve issues of triplet instability.[1,2] However, this does influence the resulting transition energies, and as a consequence the predicted absorption spectra are affected. As these systems are singlets, there is no triplet instability to account for, and the TDA negatively impacts predicted absorption. Turning off the approximation and comparing augmentated vs non-augmented Dunning's basis sets in **b)** shows that the addition of diffuse basis functions is worth the additional expense, with a shift in the peak at 550 nm by apparent when comparing the cc-pVTZ and aug-cc-pVTZ basis sets, with augmentation shifting the wavelength from 548 to 562 nm. However, the spectra obtained using aug-cc-pVDZ and aug-cc-pVTZ are almost indistinguishable, with wavelengths differing by a total of 0.023 % across the 10 excitations. Therefore, we concluded that the additional computational expense of running calculations with aug-cc-pVTZ was not required, with aug-cc-pVDZ used for all UV-Visible spectra predictions in this study.

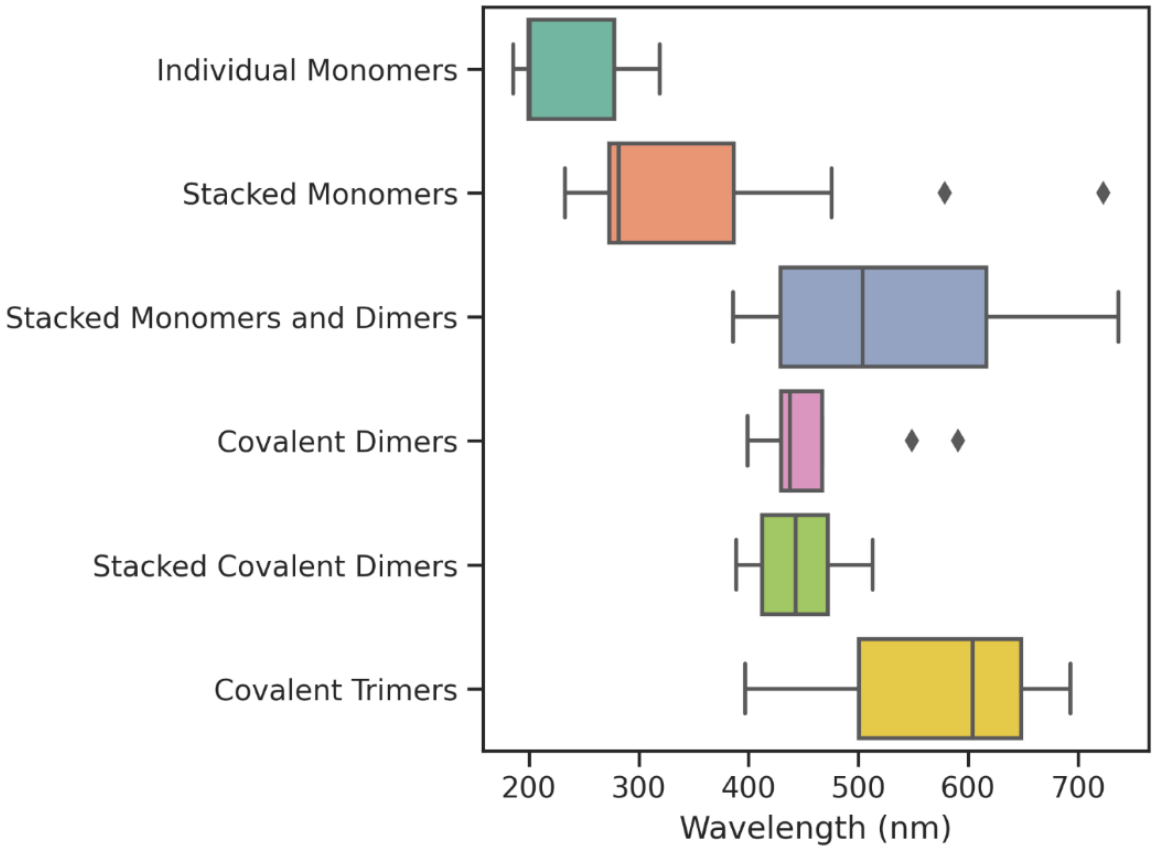
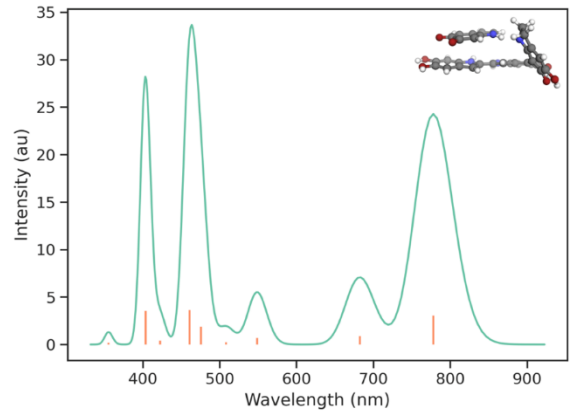
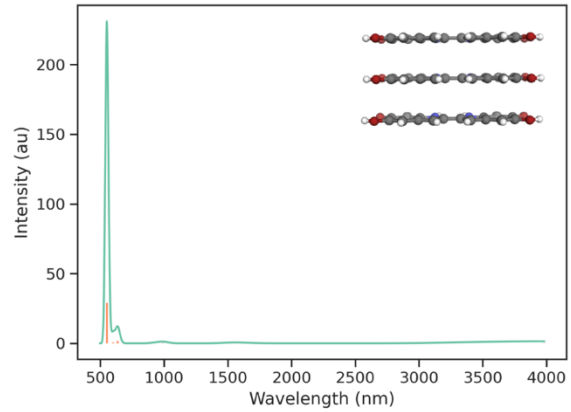


Figure S18: Box and whisker plot of distribution of the predicted wavelengths with maximum intensity across all predicted structures.

a)



b)



c)

Wavelength (nm)	Intensity (au) (Oscillator strengths of transition dipole moments)
3984.2	0.181
1563.3	0.070
988.0	0.144
916.3	0.041
664.1	$5x10^{-5}$
636.6	1.447
603.6	0.438
599.1	0.549
571.4	0.041
550.7	28.943

Figure S19: Predicted UV-Visible spectra of **a)** Trimer 1 (figure S10, structure p) with IQ (figure 11, structure a) and **b)** a triple-stacked arrangement of Z-isomers of covalent dimers (figure S10, structure h). Orange vertical lines show the wavelengths and intensities predicted by Orca, while the green curves show the summation of gaussian peaks applied to the raw data. **c)** Tabulated data of the facet **b)** showing absorption well beyond the UV-Visible range.

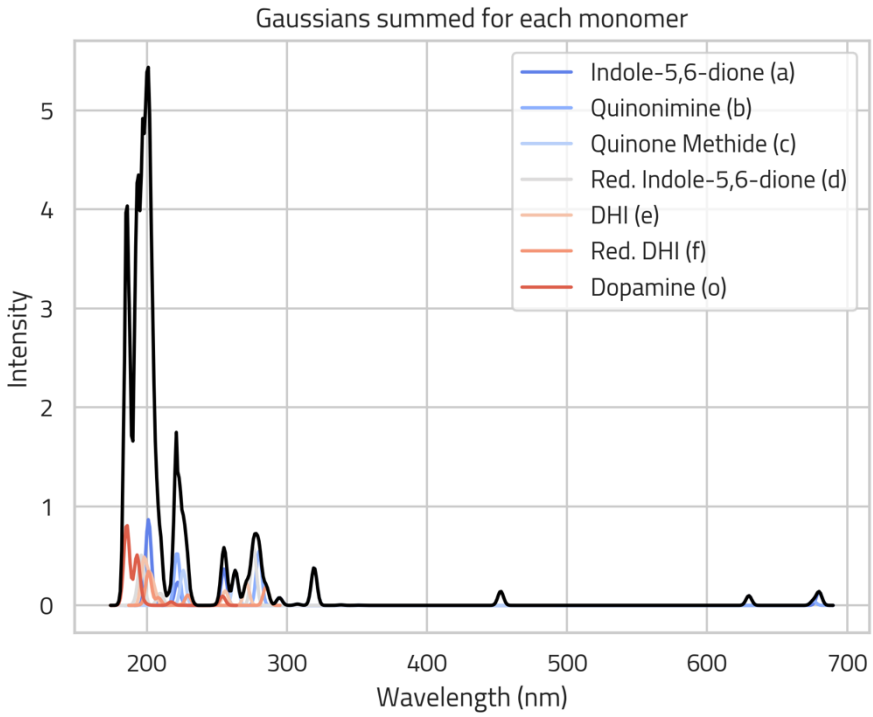


Figure S20: *Predicted spectra for individual monomers shown in varying colours. The summed spectrum over all monomers is shown in black.*

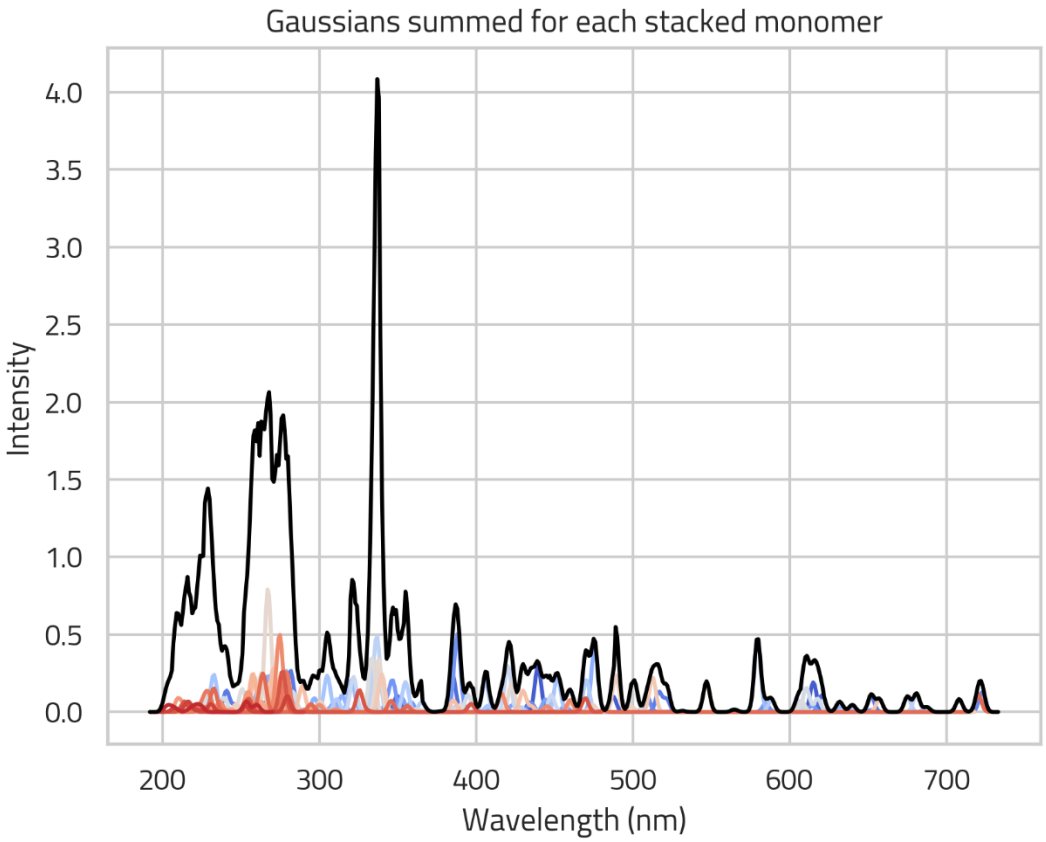


Figure S21: Predicted spectra for stacked monomers shown in varying colors. The summed spectrum over all structures is shown in black. Labels have been removed as there were 27 structures and the legend masks the plot.

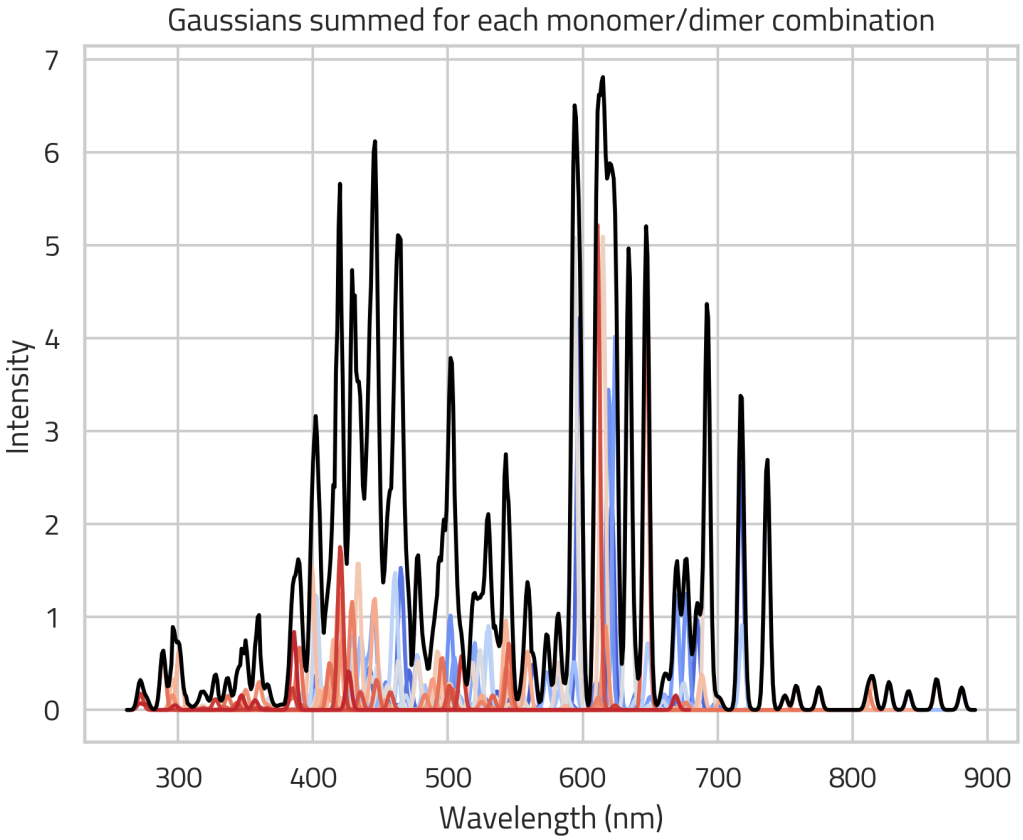


Figure S22: Predicted spectra for stacked configurations of monomers and covalent dimers shown in varying colors. The summed spectrum over all structures is shown in black. Labels have been removed as there were 30 structures and the legend masks the plot. Here 2 monomers and one covalent dimer were included.

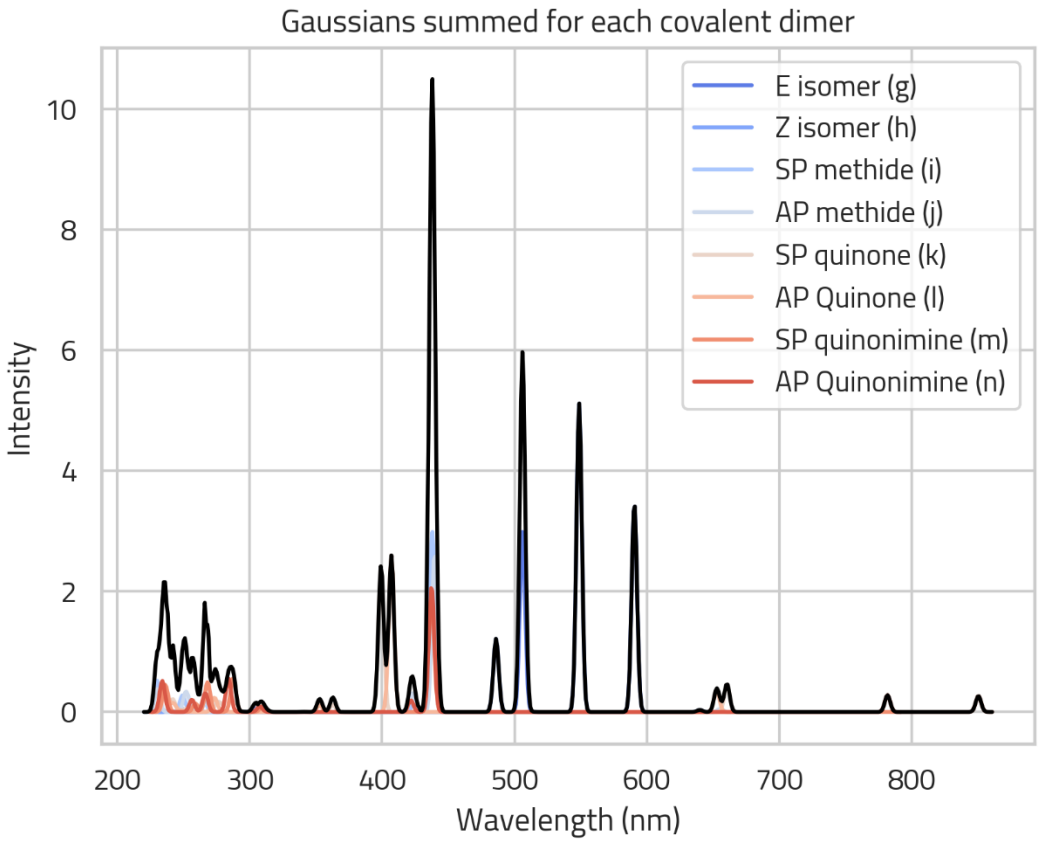


Figure S23: Predicted spectra for individual covalent dimers shown in varying colors. The summed spectrum over all structures is shown in black.

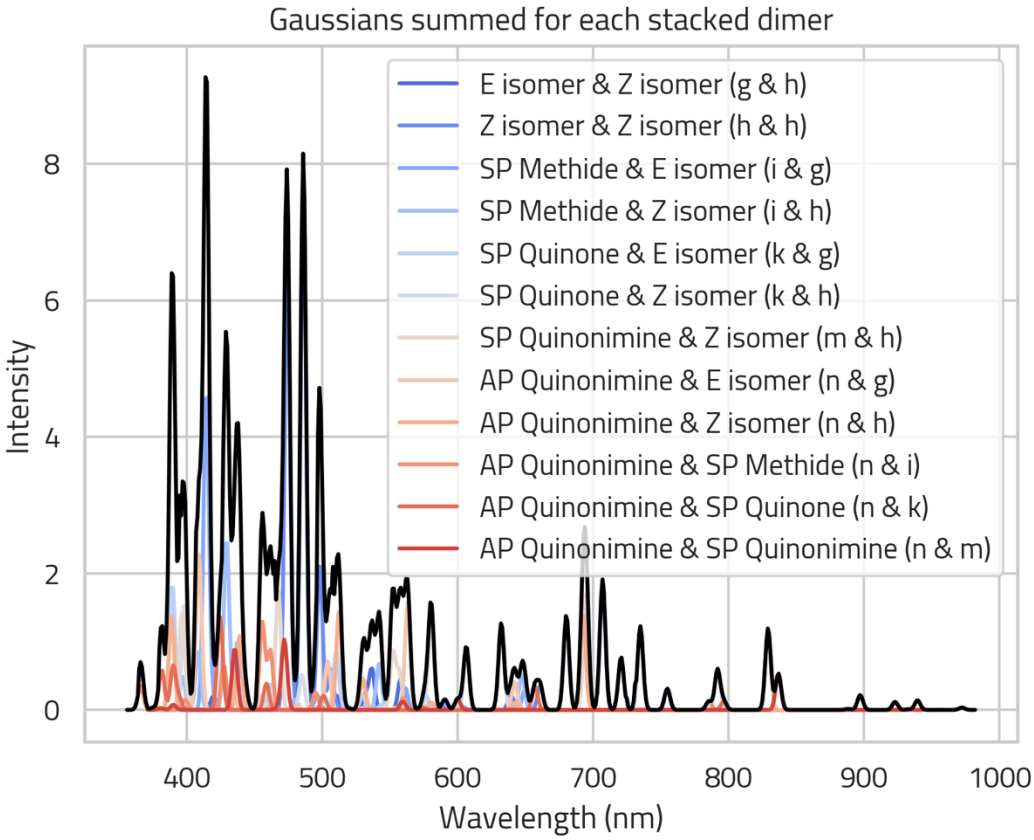


Figure S24: Predicted spectra for stacked configurations of two covalent dimers shown in varying colors. The summed spectrum over all structures is shown in black.

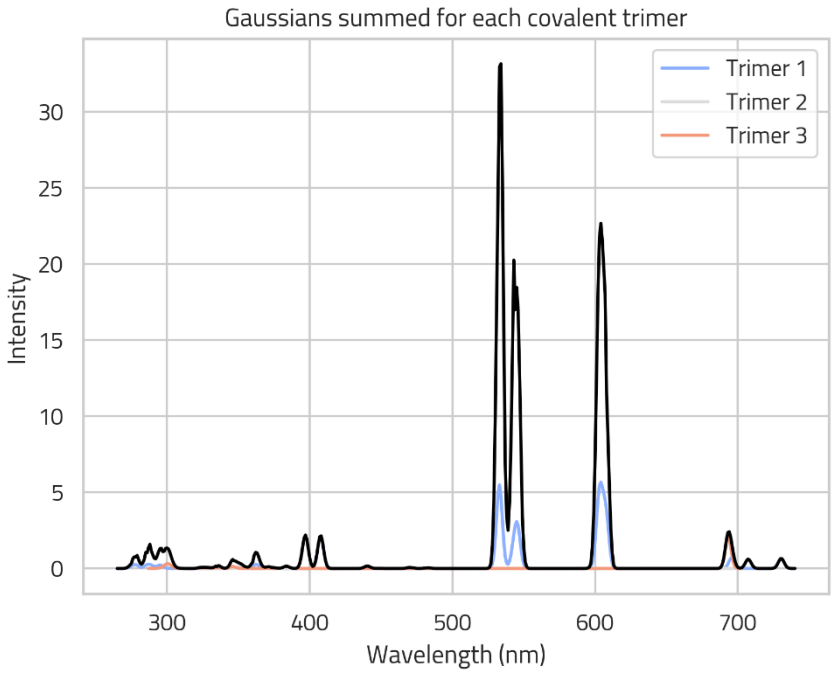


Figure S25: Predicted spectra for each covalent trimer shown in varying colors. The summed spectrum over all structures is shown in black.

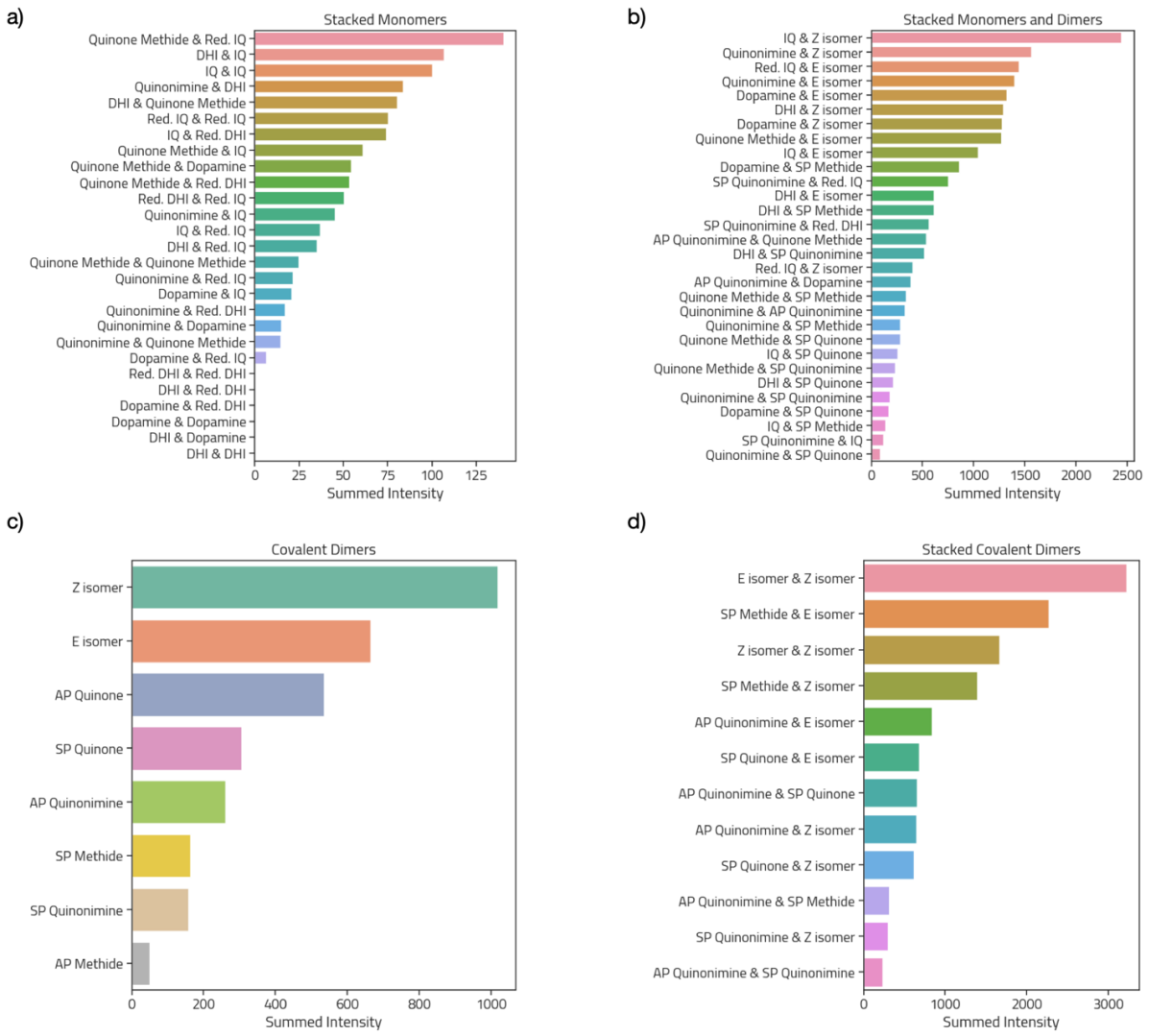


Figure S26: Summed intensities of predicted UV-Visible spectra of **a)** each stacked monomer, **b)** pairs of stacked monomers and dimer, **c)** each individual covalent dimer and **d)** pairs of stacked covalent dimers, calculated by summing gaussian intensities within 10 nm of the desired experimental peaks. Graphs show the summed intensities of peaks in predicted UV-Vis spectra within ± 10 nm of the experimentally-determined peaks at 420, 490, 530, 620, 660 and 734 nm. These were plotted to find structures that contribute most heavily to the concentrations plotted in Fig 4C in main text.

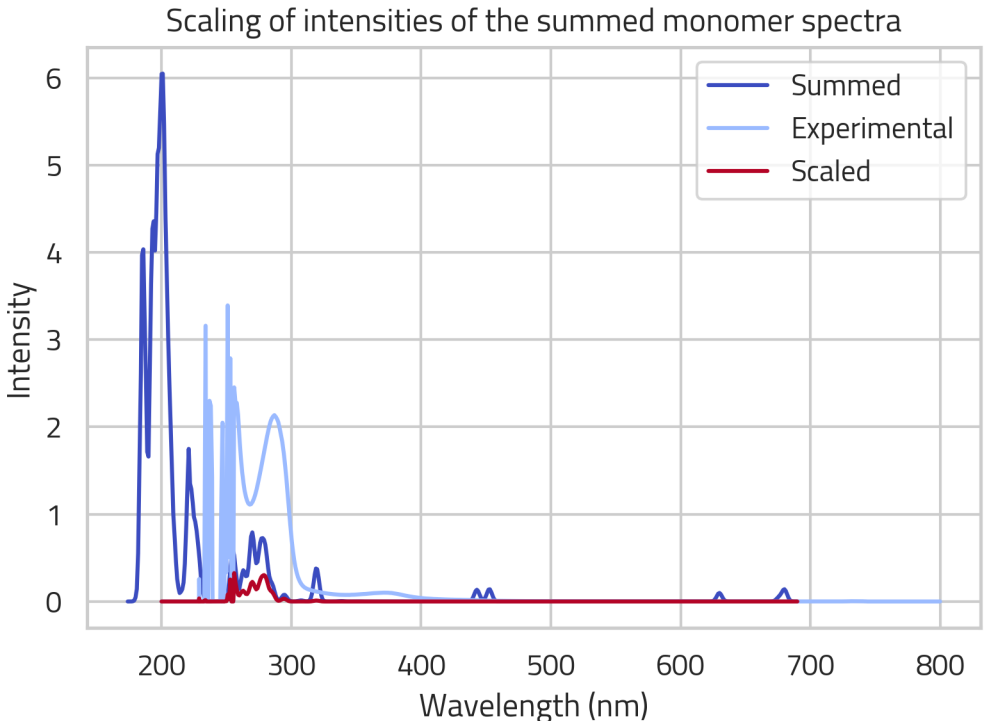


Figure S27: Scaling of summed gaussians to reflect experimental intensity. Here the experimental spectrum was taken immediately as the heating was applied (at the 7th day mark).

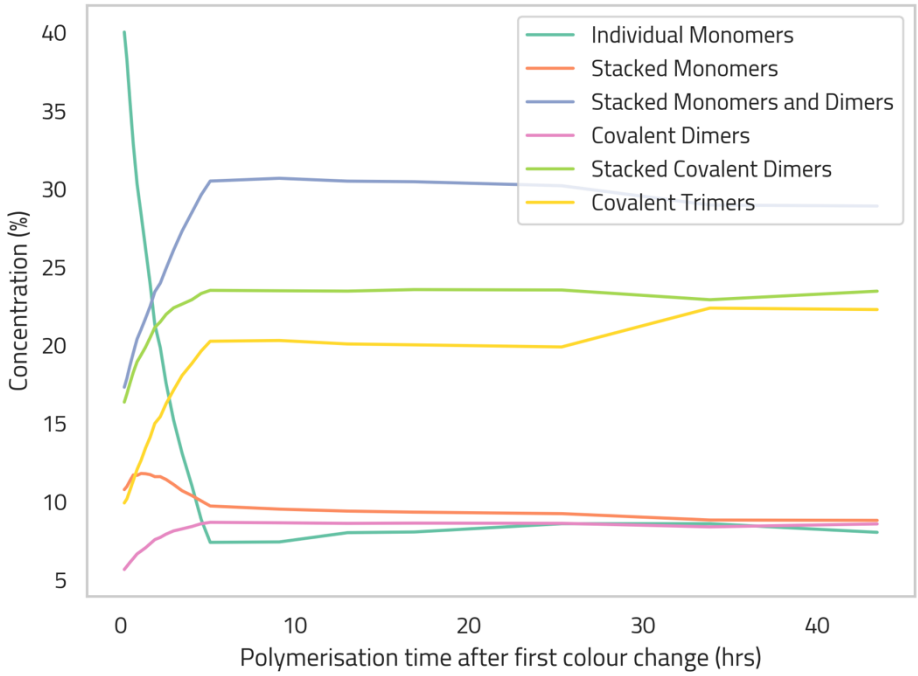


Figure S28*:* Concentrations of each structure type over the time for which the polymerization solution was heated. Concentrations are given as a percentage of the full integral for each time. Values are plotted as a five-point rolling average.

Table S3: Predicted absorbance within 5 nm of each of the peaks found to exist at different stages of the polymerisation. Note that the intensity values are the oscillator strengths as described by transition electric dipole moments, not intensity of gaussian peaks added after the calculations were performed.

Desired peak (nm)	Structural Arrangement	Molecules	Predicted Wavelength (nm)	Predicted Intensity (au)
420	Stacked Monomers	Quinone Methide & Red. Indole-5,6-dione	420.8	0.109
		Quinonimine & Red. Indole-5,6-dione	423.6	0.016
490	Stacked Monomers	2 x Indole-5,6-dione	487.9	0.032
		DHI & Indole-5,6-dione	489.7	0.075
530	Stacked Monomers and Dimers	Quinone Methide & E-isomer	530.1	0.254
		Quinone Methide & SP Methide	530.7	0.264
	Stacked Dimers	AP Quinonimine & Z-isomer	530.6	0.133
620	Stacked Monomers	2 x Indole-5,6-dione	615.6	0.048
		Quinone Methide & Red. DHI	618.3	0.022
		Indole-5,6-dione & Red. Indole-5,6-dione	621.2	0.027
	Stacked Monomers and Dimers	Indole-5,6-dione & E-isomer	622.0	0.555
		DHI & Z-isomer	615.4	1.275
		Quinonimine & E-isomer	619.8	0.865
660	Covalent Dimers	SP Quinone	660.0	0.111
		AP Quinone	653.3	0.087
	Stacked Monomers and Dimers	Quinonimine & SP Quinone	660.9	0.040
		Dopamine & SP Quinone	669.4	0.036

734	Stacked Covalent Dimers	SP Quinone & E-isomer	735.4	0.255
	Stacked Monomers and Dimers	Quinone Methide & E-isomer	737.2	0.568
	Stacked Monomers	Dopamine & Indole-5,6-dione	720.8	0.024
	Covalent Trimers	Trimer 1	730.9	0.139

References:

1 S. Hirata, M. Head-Gordon, *Chem. Phys. Lett.* 1999, **314**, 291–299.

2 A. Chantzis, A. D. Laurent, C. Adamo, D. *J.* Jacquemin, *Chem. Theory Comput.*, 2013 **9**, 4517–4525.