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

Electronic Supplementary Information for:

Experimental and Computational Evaluation of the Barrier to Torsional Rotation in a Butadiyne-Linked Porphyrin Dimer

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Attached ZIP file: optimised coordinates and energies (B3LYP/6-31G*/LANL2DZ) for **P2** (model **1d**) at 2.5° increments of butadiyne torsion; ditto for perpendicular and planar diphenyldiacetylene (B3LYP/6-31G*), tolane (B3LYP/6-31G*) and P2 (model **1e**) (B3LYP/6-31G*). In addition, the optimised excited state geometry of **1e** (S_1 state, TD-B3LYP/6-31G*) and energy are given.

UV-Vis extinction coefficients and peak maxima of P2 in DCM/THF/pyridine 10/10/1:

$\lambda_{max}(\log_{10} \varepsilon)$: 741 (5.072), 674 (4.891), 588 (4.338), 495 (5.291), 459 (5.592).

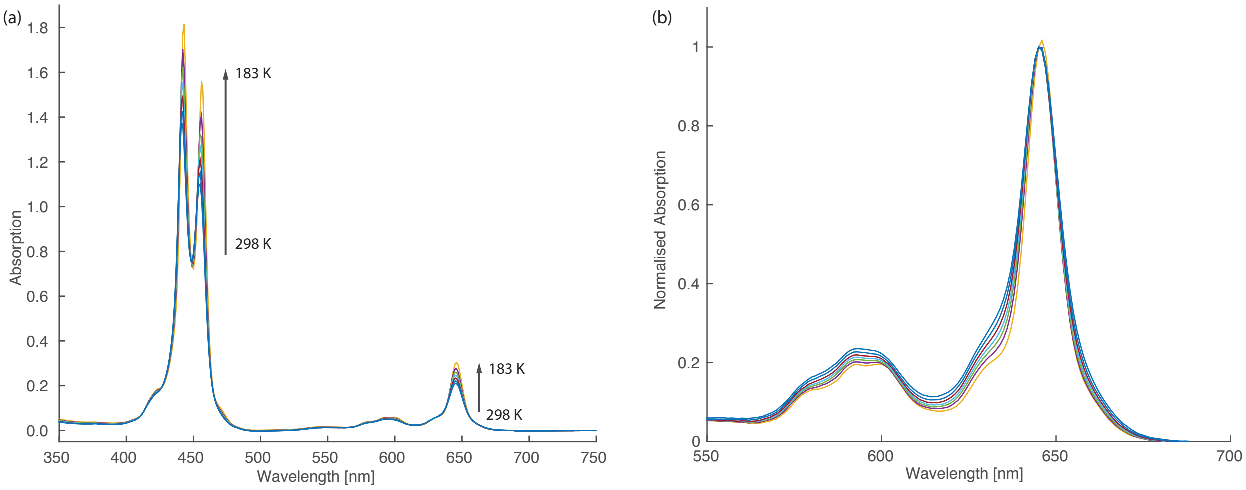


Figure S1: VT UV-Vis spectra of monomer **P1** in DCM/THF/pyridine 10/10/1, (a) full spectrum in temperature range 298–77 K (b) expansion of Q-band region in temperature range 298–163 K.

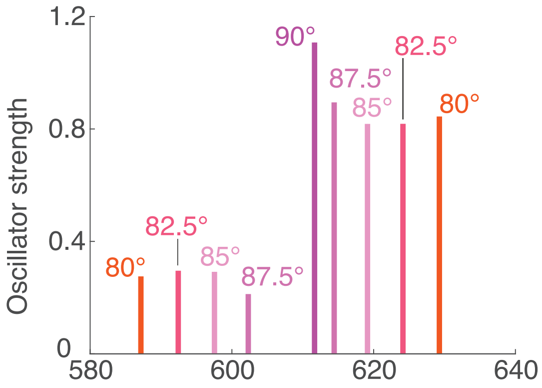
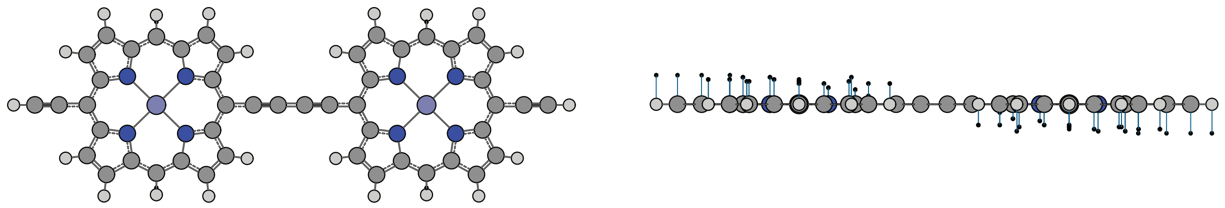
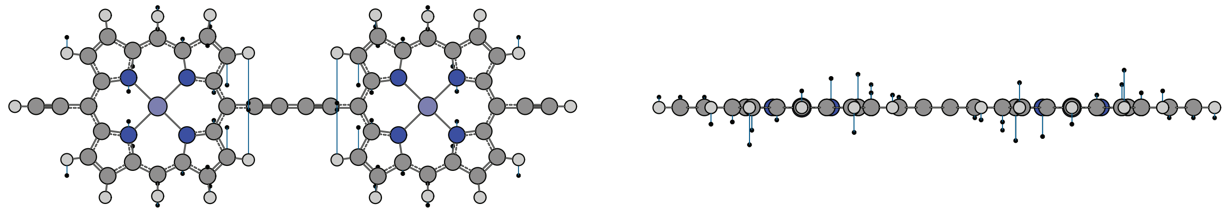


Figure S2: TD-DFT (B3LYP/6-31G*/LANL2DZ) calculated excitation energies and oscillator strengths for **P2** (model **1d**) as a function of inter-porphyrin torsion angle.

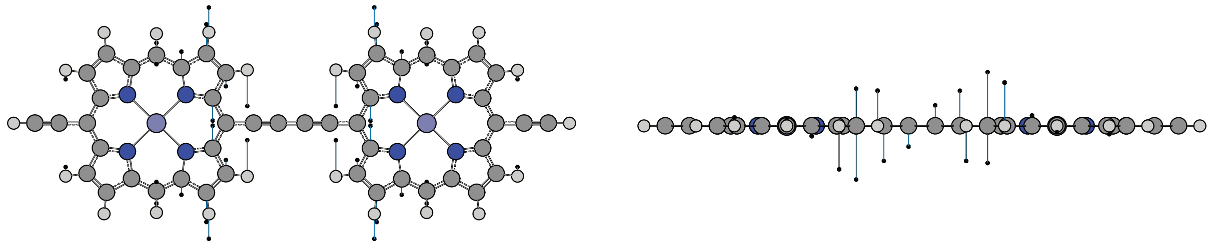
Mode 12: 75 cm^{-1}



Mode 55: 391 cm^{-1}



Mode 116: 816 cm^{-1}



Mode 179: 1345 cm^{-1}

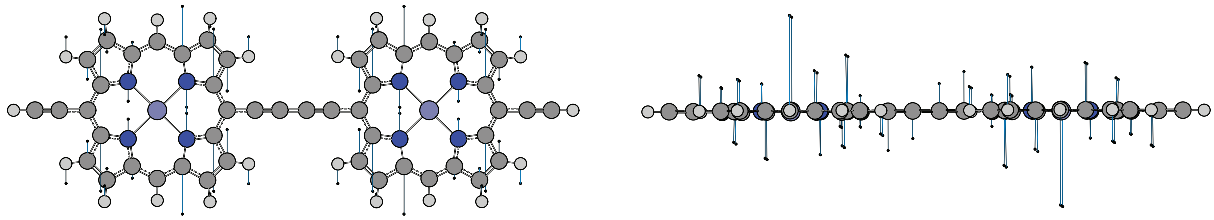


Figure S3: Normal modes of S_1 state of **P2** (model **1e**) associated with major vibronic bands (main text Figure 6).

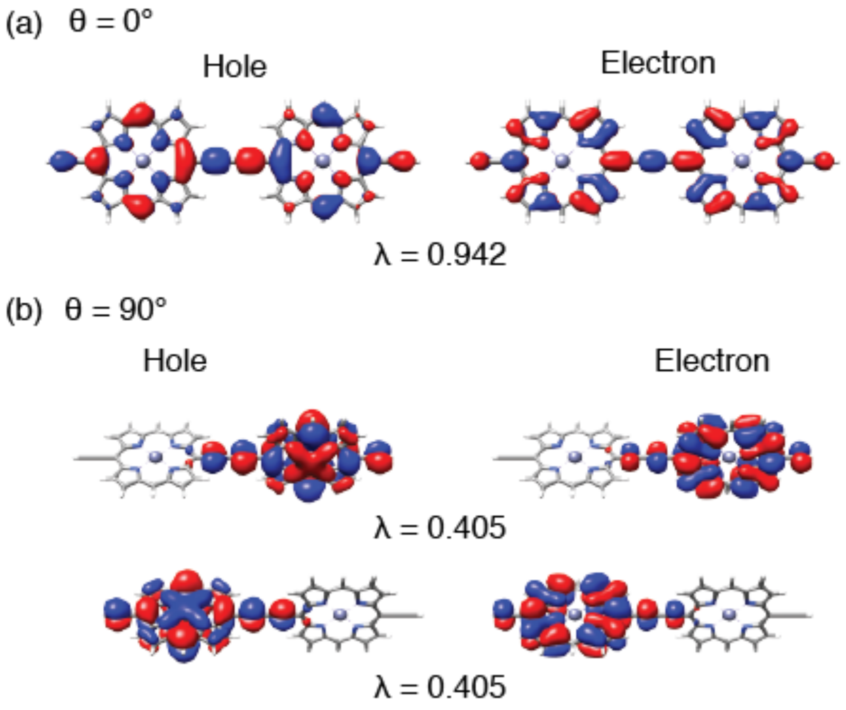


Figure S4: Natural transition orbitals (NTOs) for S_0–S_1 transition calculated (TD-B3LYP/6-31G*) for model **1e**. The eigenvalue associated with each NTO hole/electron pair is shown as λ .

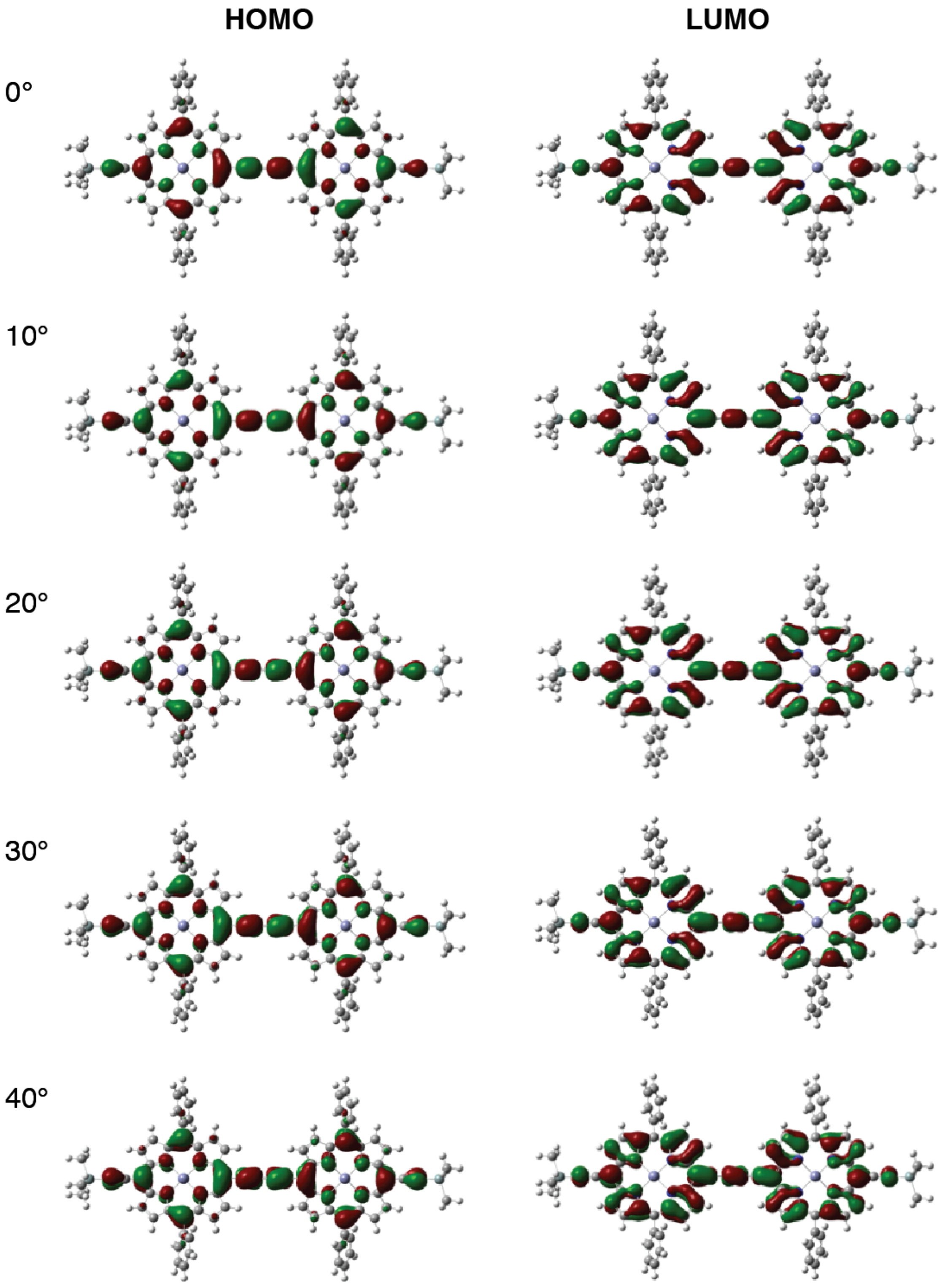


Figure S5: DFT (B3LYP/6-31G*/LANL2DZ) HOMO and LUMO for **P2** (model **1d**) as a function of interporphyrin torsion angle, 0–40°.

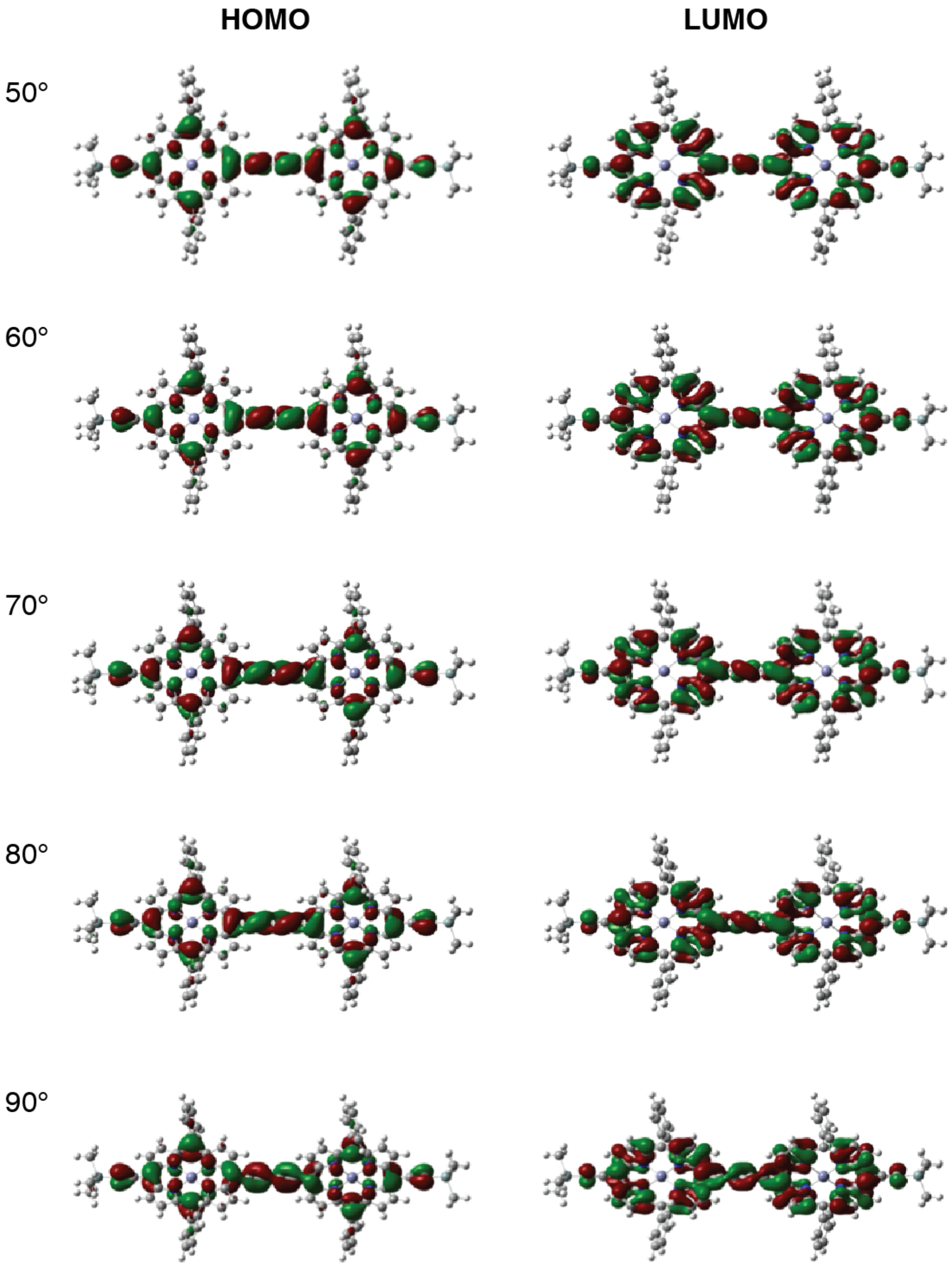


Figure S6: DFT (B3LYP/6-31G*/LANL2DZ) HOMO and LUMO for **P2** (model **1d)** as a function of interporphyrin torsion angle, 50–90°.

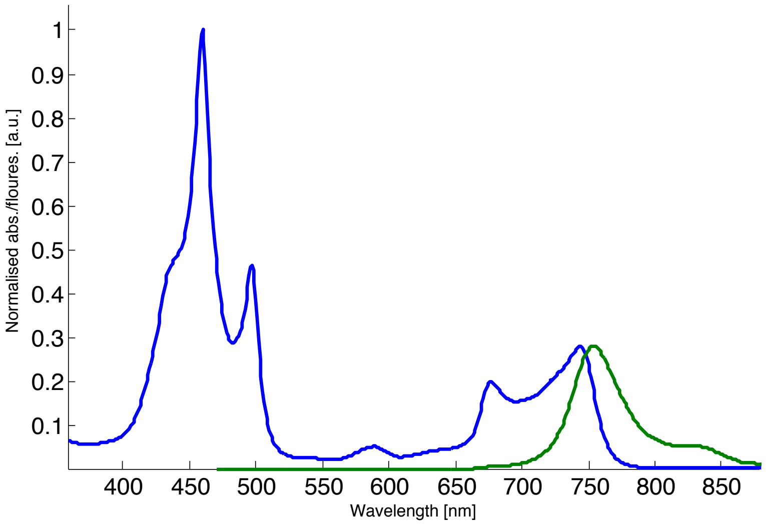


Figure S7: Absorption (blue) and fluorescence (green) of **P2** (CHCl$_3$ + 1% pyridine). λ_{ex} = 450 nm.

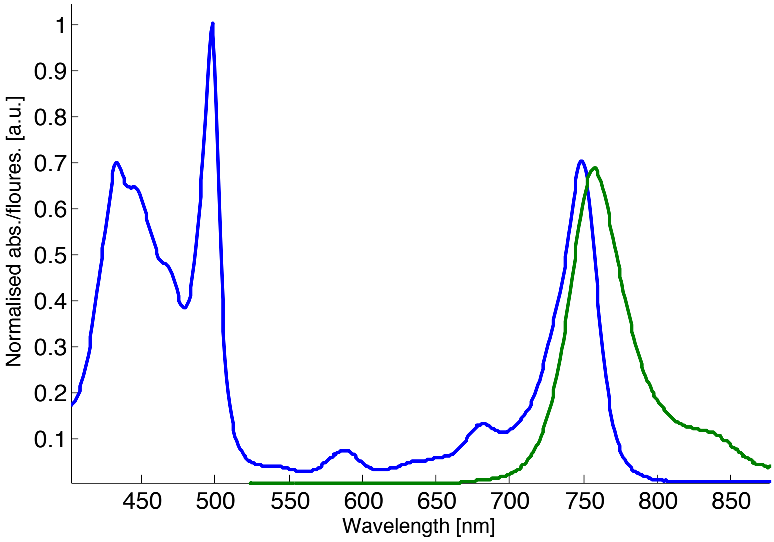


Figure S8: Absorption (blue) and fluorescence (green) of **P2•T2** (CHCl$_3$). λ_{ex} = 450 nm. λ_{max}(log$_{10}$ ε): 749 (5.297), 682 (4.574), 588 (4.324), 498 (5.452), 434 (5.295).

The experimental ratio of extinction coefficients for planar and perpendicular conformers ($\varepsilon_{/\!/}/\varepsilon_{\perp}$) was estimated by comparing the absorption coefficients of free **P2** (in the presence of pyridine) and complexed **P2•T2** at 750 nm (planar, $\varepsilon_{/\!/}$) and 675 nm (perpendicular, $\varepsilon_{\perp}$), after subtraction of the vibronic contribution at 675 nm in free **P2**. The vibronic contribution in liquid solution at room temperature is given by the following equation, assuming that in **P2•T2**, there is no perpendicular **P2** (*i.e.*, all absorption at 675 nm arises from the vibronic contribution).

$$x_{vibr} = \frac{\varepsilon_{675\ nm,\ T2}}{\varepsilon_{750\ nm,\ T2}} = 0.171$$

Thus $\varepsilon_{\perp}$ can be estimated by subtracting this vibronic contribution:

$$\varepsilon_{\perp\ ,\ py} = x_{vibr} \times \varepsilon_{675\ nm,\ py} = 60960\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$$

Where ε_{py} corresponds to spectra recorded in the presence of pyridine, and ε_{T2} to the complex **P2•T2**. Next we calculate and $\Delta\varepsilon_{/\!/}$. $\Delta\varepsilon_{\perp}$ was found in the previous step (60960 M^{-1} cm^{-1}), assuming all of the perpendicular **P2** has been planarised.

$$\Delta\varepsilon_{/\!/} = \varepsilon_{750\ nm,\ T2} - \varepsilon_{750\ nm,\ py} = 103990\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$$

Thus:

$$\frac{\Delta\varepsilon_{/\!/}}{\Delta\varepsilon_{\perp}} = \frac{103990}{60960} = 1.7059$$