**Electronic Supplementary Information for:**

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

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**Table of Contents**

**UV-Vis extinction coefficients and peak maxima of P2 in DCM/THF/pyridine 10/10/1:** S2

**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. S2

**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. S2

**Figure S3:** Normal modes of S1 state of P2 (model 1e) associated with major vibronic bands (main text Figure 6). S3

**Figure S4:** Natural transition orbitals (NTOs) for S0–S1 transition calculated (TD-B3LYP/6-31G*) for model 1e. The eigenvalue associated with each NTO hole/electron pair is shown as λ. S4

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

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

**Figure S7:** Absorption (blue) and fluorescence (green) of P2 (DCM + 1% pyridine). λex = 450 nm. S7

**Figure S8:** Absorption (blue) and fluorescence (green) of P2•T2 (DCM). λex = 450 nm. S7

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 (S1 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:

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

**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.
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 $\lambda$. 

(a) $\theta = 0^\circ$

(b) $\theta = 90^\circ$
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 (CHCl₃ + 1% pyridine). λₑₓ = 450 nm.

Figure S8: Absorption (blue) and fluorescence (green) of P2•T2 (CHCl₃). λₑₓ = 450 nm. λ_max(log₁₀ 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 (ε / ε⊥) was estimated by comparing the absorption coefficients of free P2 (in the presence of pyridine) and complexed P2•T2 at 750 nm (planar, εₚ) and 675 nm (perpendicular, ε⊥), 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).

\[ x_{vibr} = \frac{\epsilon_{675 \text{ nm}, T2}}{\epsilon_{750 \text{ nm}, T2}} = 0.171 \]

Thus ε┴ can be estimated by subtracting this vibronic contribution:

\[ \epsilon_{\perp, py} = x_{vibr} \times \epsilon_{675 \text{ nm}, py} = 60960 \text{ M}^{-1} \text{ cm}^{-1} \]

Where εpy corresponds to spectra recorded in the presence of pyridine, and εT2 to the complex P2•T2. Next we calculate and Δεpy, Δε┴ was found in the previous step (60960 M⁻¹ cm⁻¹), assuming all of the perpendicular P2 has been planarised.

\[ \Delta \epsilon_{\parallel} = \epsilon_{750 \text{ nm}, T2} - \epsilon_{750 \text{ nm}, py} = 103990 \text{ M}^{-1} \text{ cm}^{-1} \]

Thus:

\[ \frac{\Delta \epsilon_{\parallel}}{\Delta \epsilon_{\perp}} = \frac{103990}{60960} = 1.7059 \]