

The Solvent Dependent Photophysics of Diphenyloctatetraene

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1. Franck-Condon Modelling

The vibronic structure within experimental absorption and fluorescence of DPO in solution were modelled using a simple displaced harmonic oscillator Franck-Condon model, as previously outlined in refs. ^{1,2}. The model relies on the following assumptions: (i) electronic transitions couple to a single dominant vibrational mode; (ii) all vibronic peaks have the same full-width half-maximum; (iii) the associated line shape for all peaks is the same and Gaussian; (iv) the Franck-Condon progression ignores effects of anharmonicity.

The intensity of the vibronic progressions should follow a Poisson distribution, as described by Equations S1 and S2 for fluorescence and absorption respectively:

$$I_{Fl}(E) = (n_E E)^3 \sum_m \left(e^{-S} \frac{S^m}{m!} e^{-\left(\frac{E-(E_0-m\omega_{\text{vib}})}{\sigma}\right)^2} \right) \quad (\text{S1})$$

$$I_{Abs}(E) = (n_E E) \sum_m \left(e^{-S} \frac{S^m}{m!} e^{-\left(\frac{E-(E_0+m\omega_{\text{vib}})}{\sigma}\right)^2} \right) \quad (\text{S2})$$

where, $I_{Fl}(E)$ and $I_{Abs}(E)$ are the intensity of the fluorescence and absorption as a function of energy E (in eV), and n_E is the energy dependent refractive index. ω_{vib} is the associated energy with the Franck-Condon active vibrational mode and S the associated Huang-Rhys factor, m is the vibrational quantum number, E_0 is the electronic origin associated with $m = 0$, and σ determines the Gaussian linewidth of each vibrational peak, as defined by the full-width half-maximum = $2\sigma\sqrt{2\ln 2}$.

Modelled absorption and fluorescence spectra for DPO in cyclohexane (overlaid with experimental data) are shown in Figure S1. The same parameters, $S = 1.27$, $\omega_{\text{vib}} = 0.188 \pm 0.001$ eV (1520 ± 10 cm⁻¹) and $\sigma = 140$ meV, were used to model the absorption spectra of DPO in all 10 different solvents, only altering E_0 , which is derived from experimental data (see Table

1 in main manuscript). For fluorescence spectra, good agreement with experimental data was achieved using $\omega_{\text{vib}} = 0.172 \pm 0.001$ eV (1390 ± 10 cm⁻¹) and $\sigma = 162$ meV. The electronic origin was experimentally derived, however, unlike absorption spectra, the Huang-Rhys factor for fluorescence varied between 2.27 and 2.45 between different solvents, as expected for fluorescence intensity derived from a Herzberg-Teller intensity borrowing mechanism.

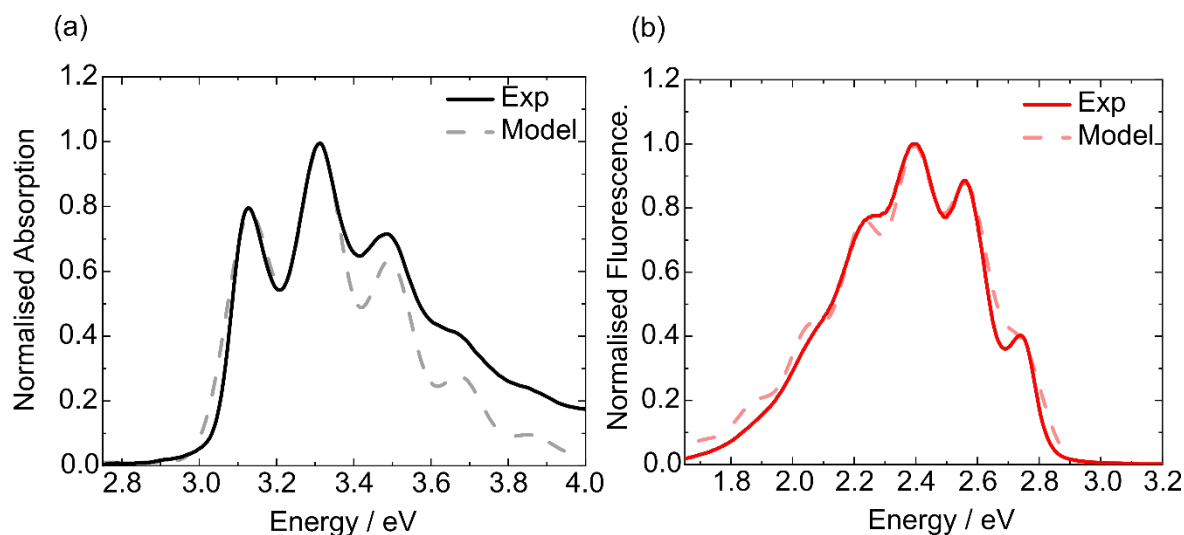


Figure S1 Comparison of steady state normalised (a) absorption and (b) fluorescence data of DPO in cyclohexane with Franck-Condon model (dashed line) of data. Details of parameters used are given in the text.

2. DFT and TD-DFT calculated minimum energy structures

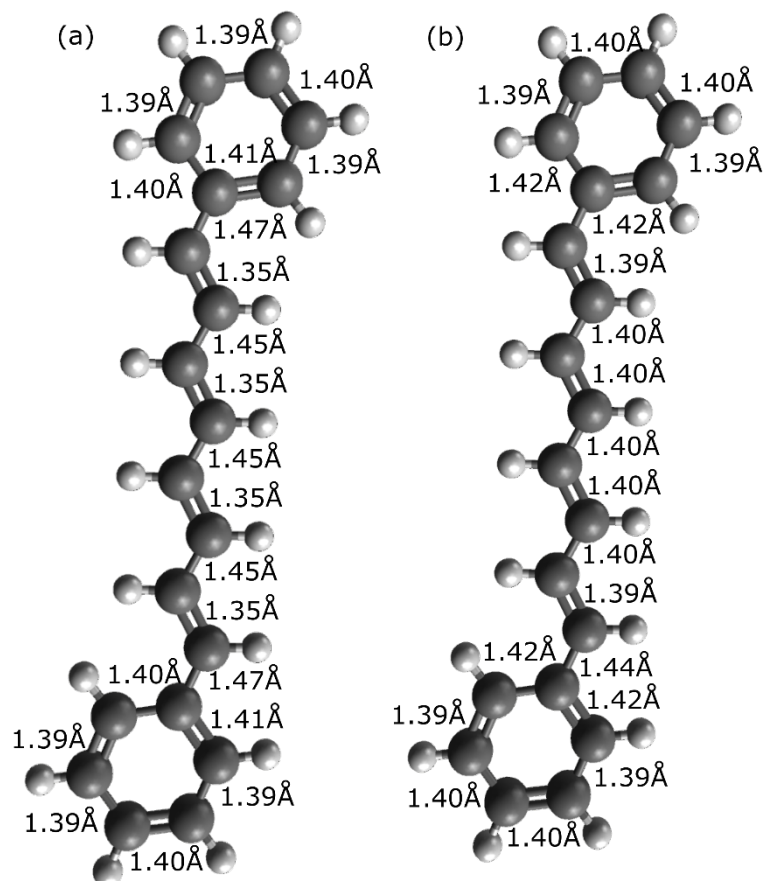


Figure S2 Minimum energy geometries of the (a) S_0 and (b) $1B_u$ states of DPO. Bond lengths associated with the polyene chain and terminal phenyl rings are overlaid.

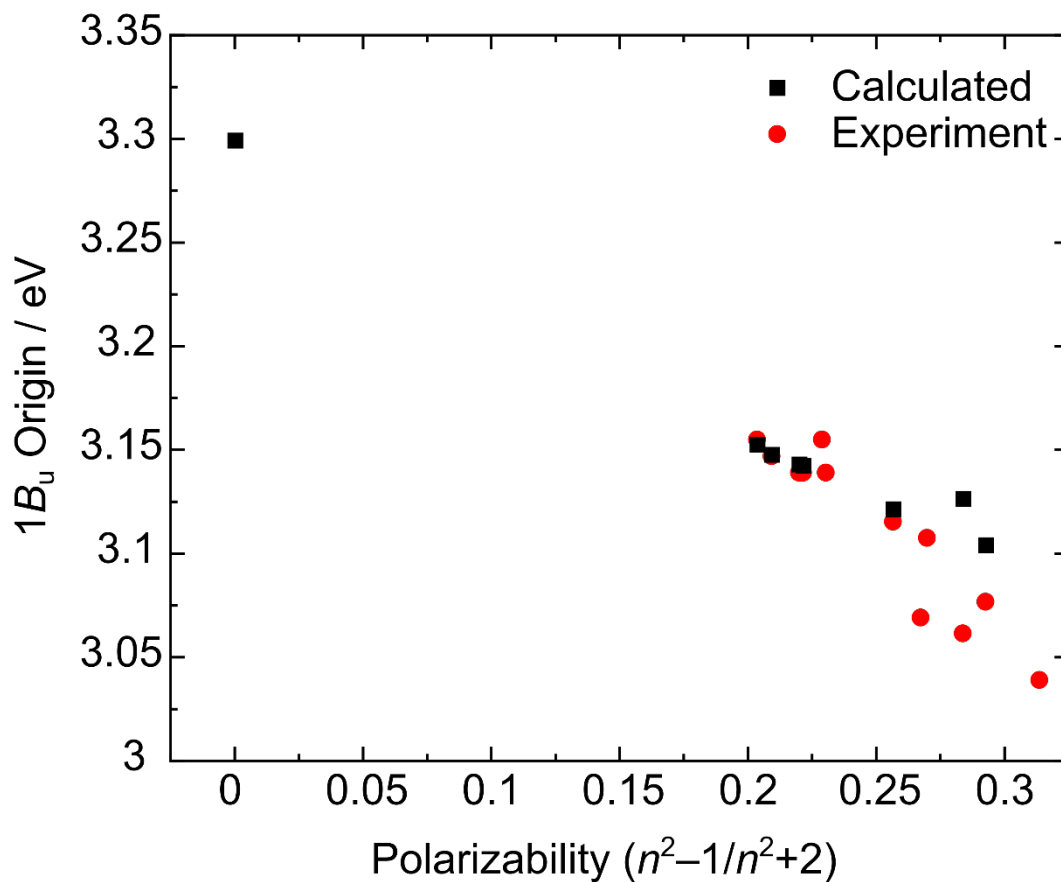


Figure S3 Comparison of experimental and calculated vertical $1B_u$ excitation energies as a function of solvent polarizability. The calculated excitation energies have been shifted by -160 meV to aid comparison.

3. Instrument Response Function

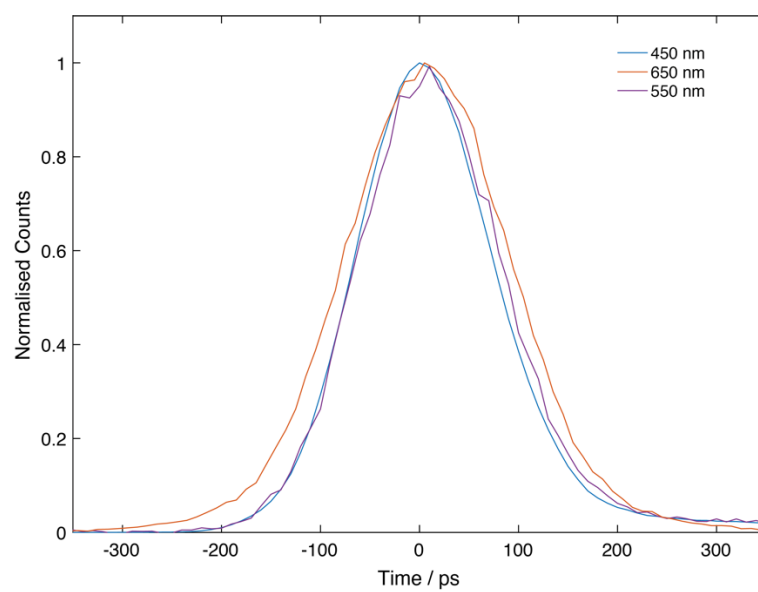


Figure S4 Instrument response function measured by solvent scatter for three displayed laser excitation wavelengths.

4. WR-TCSPC Spectra

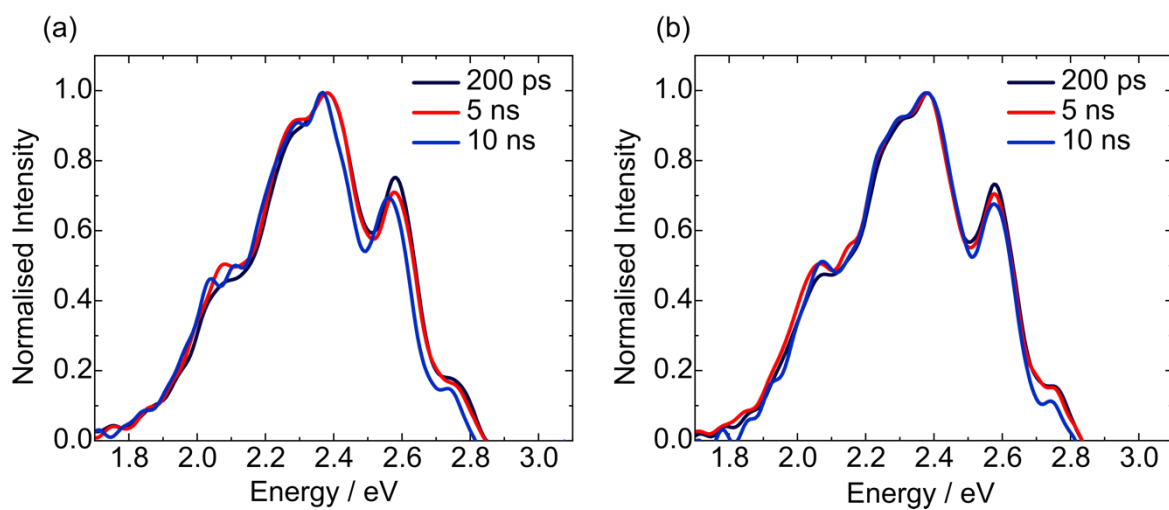


Figure S5 Normalised fluorescence spectra averaged over 200 ps windows from WR-TCSPC measurements of DPO in (a) *n*-hexane and (b) ethanol for a series of delays shown in the legend.

References

- (1) Köhler, A.; Bäessler, H. *Electronic Processes in Organic Semiconductors*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2015.
- (2) Saidani, M. A.; Benfredj, A.; Hamed, Z. B.; Romdhane, S.; Ulbricht, C.; Egbe, D. A. M.; Bouchriha, H. Franck-Condon Analysis of the Photoluminescence Spectra of a Triple-Bond Containing Polymer as a Solution and as a Thin Film. *Synth. Met.* **2013**, *184*, 83–85.