

Supplementary Information

Probing the excited state dynamics in perinone molecules for photovoltaic applications using transient absorption spectroscopy

Suman Dhama, Yogesh Kumar, Chaitrali Sengupta, Ravindra Pandey*

*Department of Chemistry, Indian Institute of Technology Roorkee, 247667 Haridwar,
Uttarakhand India*

Email: rpandey@cy.iitr.ac.in

S.I. 1. Synthesis and Characterization of Perinone (Naphthalene Bis-benzimidazole):

1,4,5,8-naphthalene tetracarboxylic dianhydride (2.1 gm) and o-phenylenediamine (1.675 gm) were mixed in 100 ml glacial acetic acid and solution was refluxed overnight and then filtered with ethanol and water several times. The red colored filtrate was dried in oven at 80°C. To separate the cis and trans isomers from the red colored powder, 1gm of powder was taken in round bottom flask and 2 gm of KOH in 25 ml of ethanol were added into it and heated at 78°C for 2 hrs. After that the solution was filtered. The filtrate contains cis isomer and residue contain trans isomer. Trans isomer was washed with ethanol and water and it turns into orange color. In filtrate acidic water was added it turns into deep red color. Both the isomers were dried in oven.^{1,2}

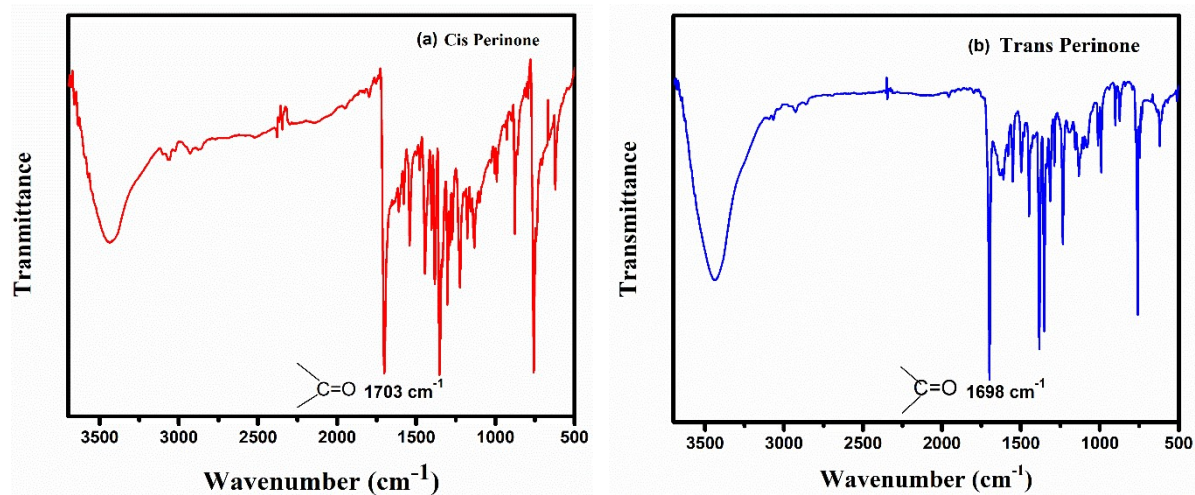


Figure S1. IR spectra of (a) Cis and (b) trans perinone taken in KBr Pellet.

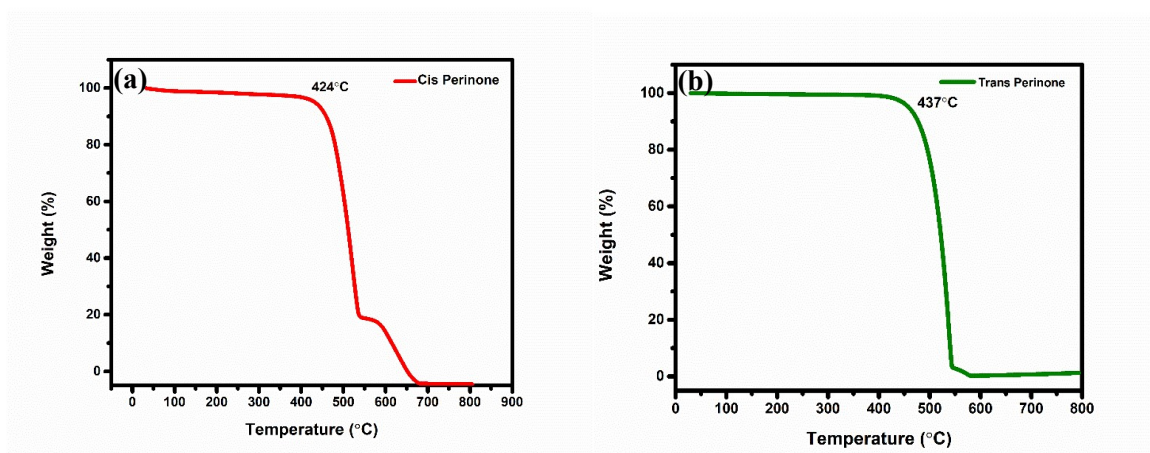


Figure S2. Thermogravimetric Analysis (TGA) of (a) cis perinone and (b) trans perinone. Melting point of cis and trans perinone are 424 °C and 437°C respectively.

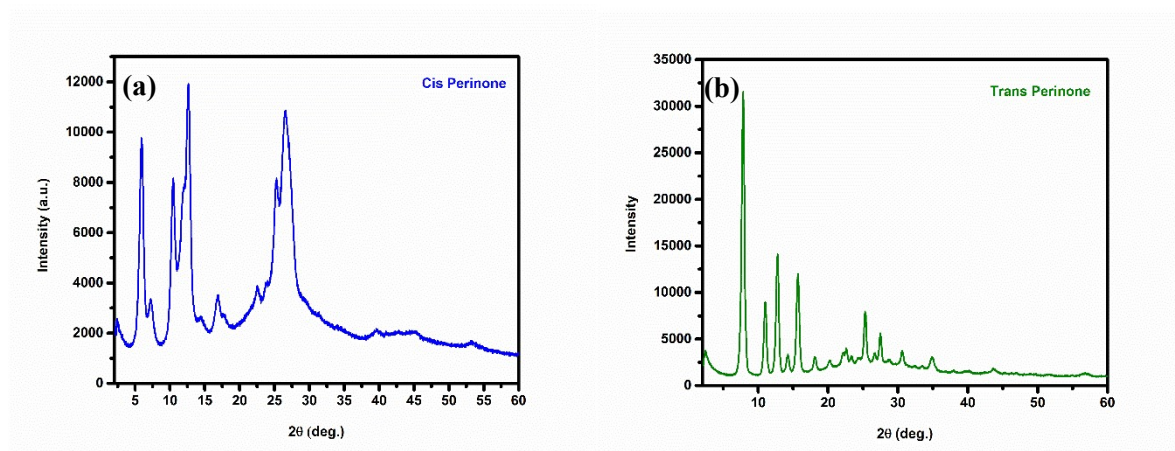


Figure S3. Powder XRD pattern of (a) *cis* perinone and (b) *trans* perinone

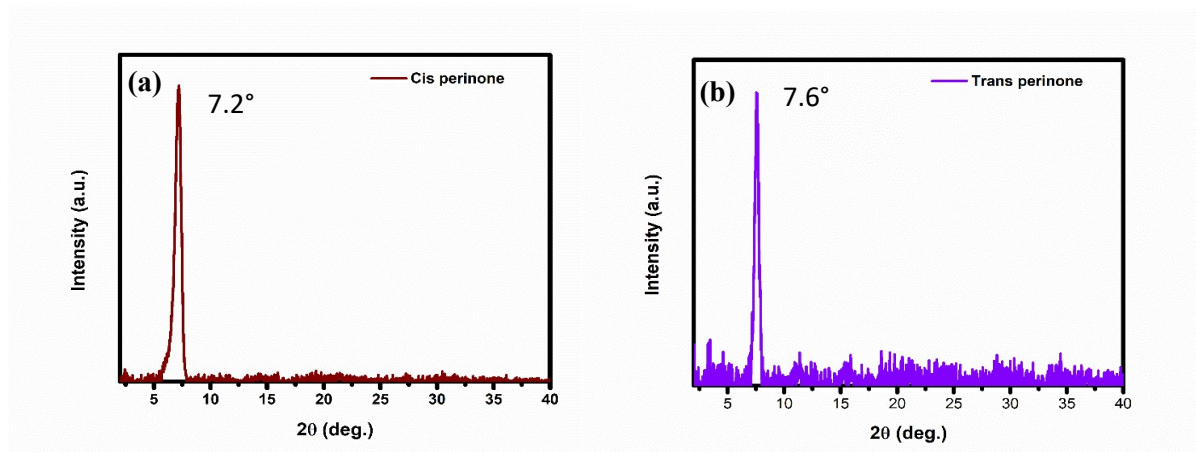


Figure S4. Thin film X ray diffraction of (a) cis perinone and (b) trans perinone

S.I. 2. We obtained single peak in TF-XRD in case of both the isomers which we used to calculate the distance between layers using Bragg's equation as follows

$$n\lambda = 2d\sin\theta$$

2θ is 7.2° and 7.6° for cis and trans perinone respectively.

The powder XRD shows multiple peaks due to its polycrystalline nature for both isomers.

S.I. 3. We have used TD-DFT calculation to obtain the S_1 and T_1 energy levels using B3LYP 6-31G basis set. The S_1 and T_1 energy levels obtained for cis perinone are 1.56 eV, 0.78 eV while for trans perinone are 2.19 eV and 1.03 eV. The gas phase calculation for S_1 energy levels considerably matches with the experimental tauc plot which gives a value of 1.95 eV for cis perinone and 2.11 eV for trans perinone.

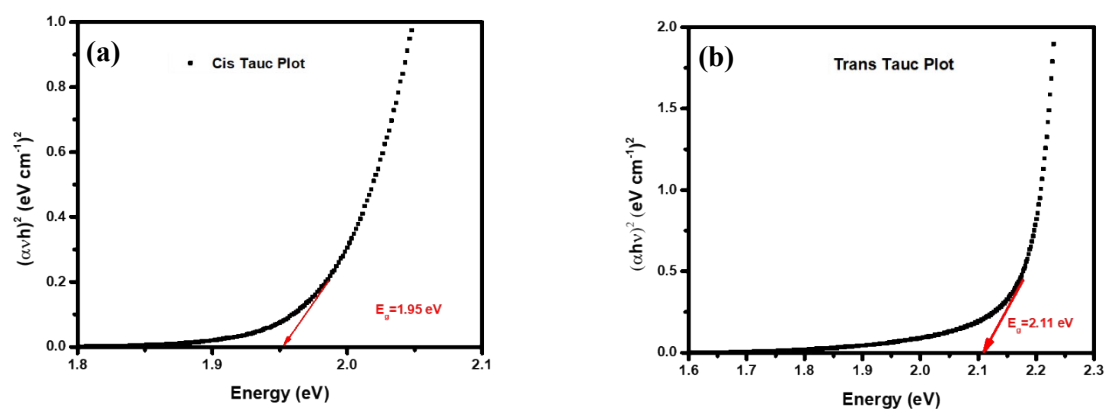


Figure S5. Tauc Plot of (a) cis and (b) trans perinone thin film

Table S1. Absorption, band gap and emission data of cis perinone in thin film

Thin Film	Absorbance (nm)	Band Gap (eV)	Fluorescence (nm)	Fluorescence Lifetime (ns)	$\chi^{(2)}$
Cis Perinone	449, 486, 521, 568	1.95	683	2.24 ± 0.05	1.19
Trans Perinone	432, 452, 491, 529	2.11	555, 628	12.7 ± 0.03	1.21

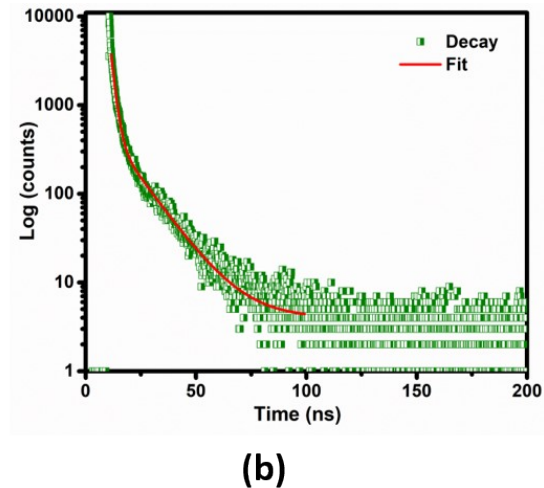
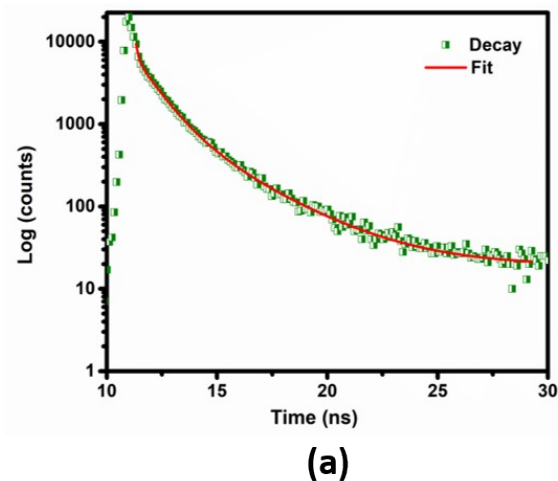


Figure S6. Fluorescence decay profile of thin films (a) *Cis Perinone* and (ii) *Trans Perinone* ($\lambda_{exc} = 463 \text{ nm}$)

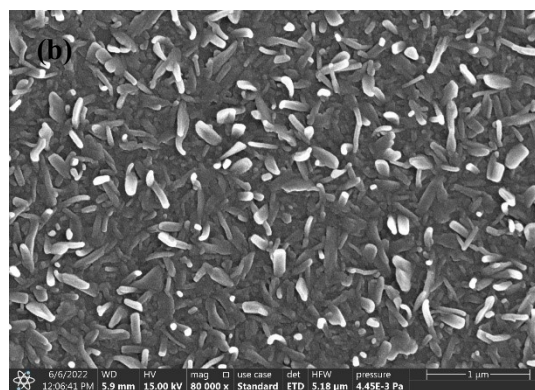
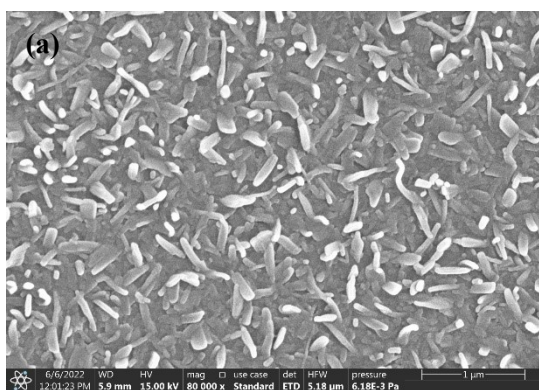


Figure S7. Field emission scanning electron microscopy images of (a) *cis perinone* and (b) *trans perinone* thin film

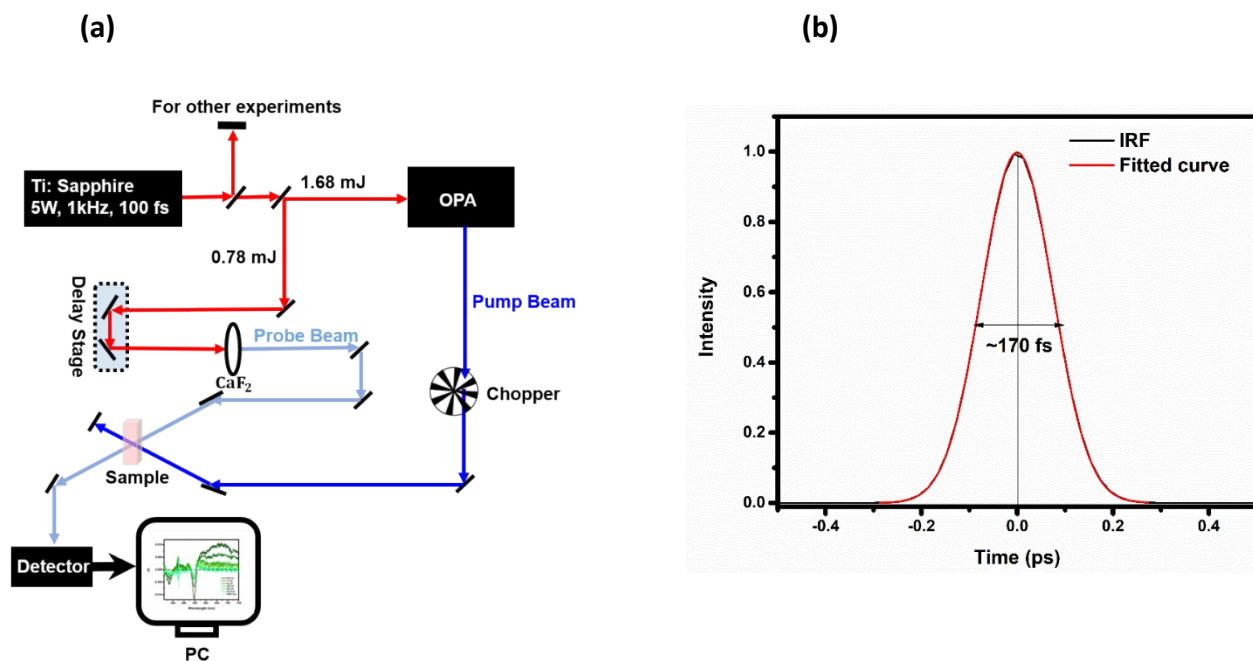


Figure S8. (a) Schematic of transient absorption spectrophotometer (b) Instrument response function of transient absorption spectrometer

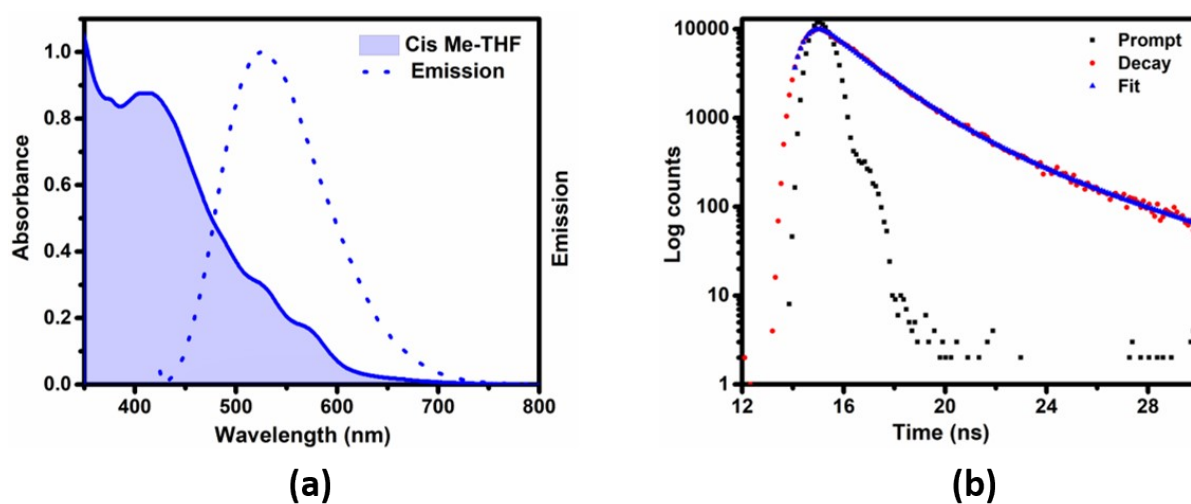


Figure S9. (a) Normalised steady state absorption (solid line), emission (dashed line) and (b) time resolved fluorescence decay profile of cis perinone in MeTHF ($\lambda_{exc} = 463$ nm)

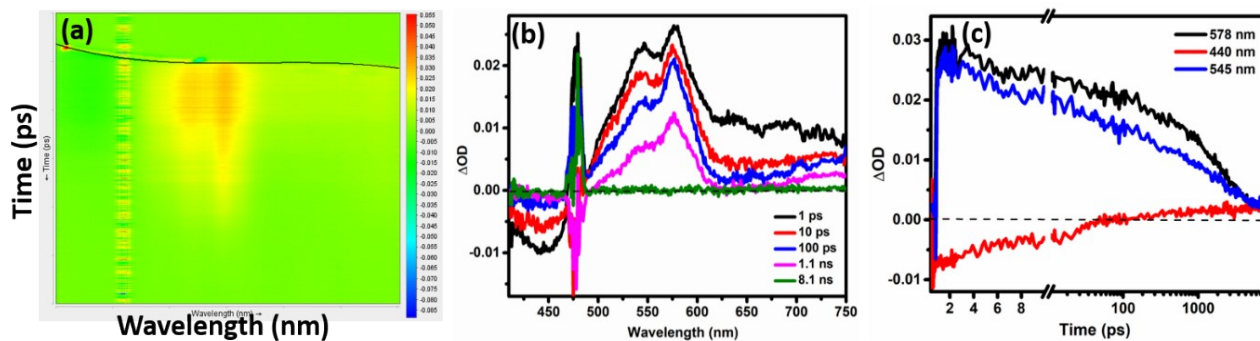


Figure S10. The fs TA profile pictures of *cis* perinone in MeTHF (A), contour plot (B) ΔOD time-gated spectra at selected delay times (C) and time traces at selected probe wavelengths respectively, after excitation at 480 nm with a low pump power ($3\text{--}5 \mu\text{J/pulse}$) to avoid multi-exciton generation and sample bleaching. The time axis is linear up to 10 ps and logarithmic thereafter.

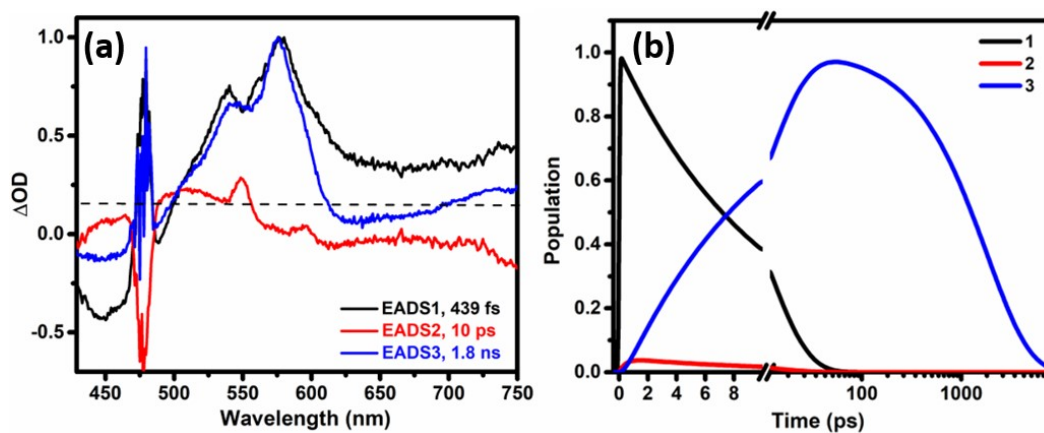
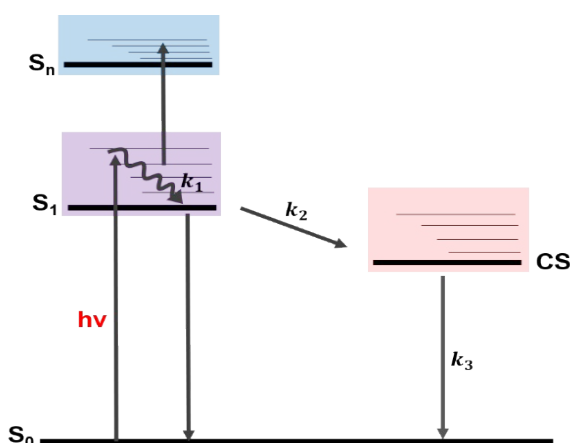


Figure S11. (a) EADS and (b) Time absorption profile of *cis* perinone in MeTHF



Scheme S1. Energy diagram for *cis* perinone in Me-THF

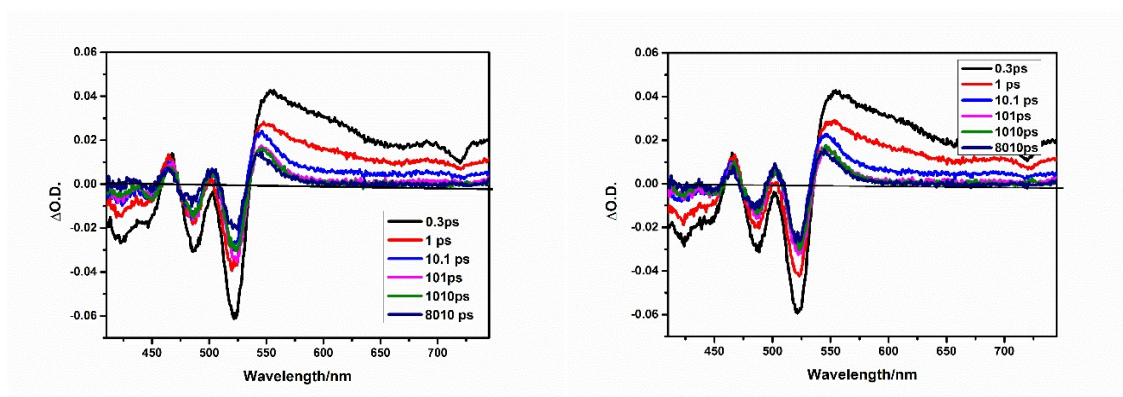


Figure S12. Another two sets data of time gated spectra of trans perinone thin film after excitation at 480 nm.

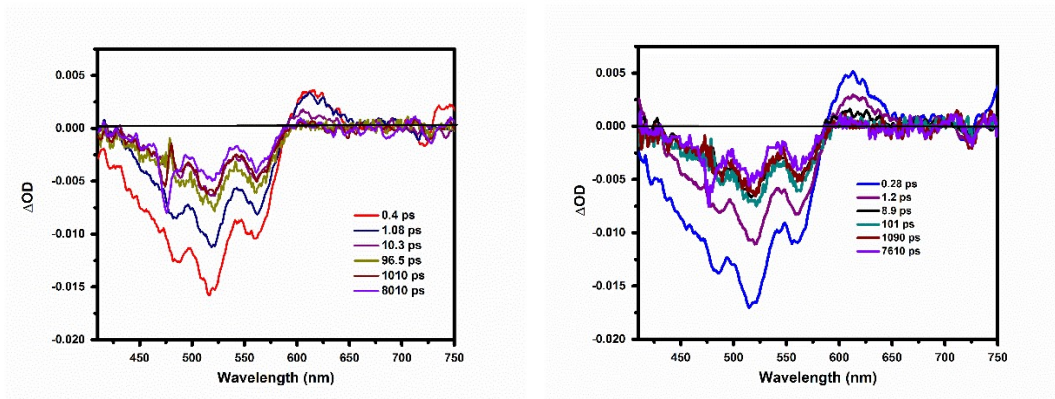


Figure S13. Another two sets data of time gated spectra of cis perinone thin film after excitation at 480 nm.

Table S2: Time constants for other two sets of data of trans and cis perinone thin films:

Thin Film	τ_1 / fs	τ_2 / ps	τ_3 / ns
Trans Perinone – Sample 2	670	29.21	19.95
Trans Perinone – Sample 3	730	23.67	18.27
Cis Perinone – Sample 2	1.05	10.10	17.69
Cis Perinone – Sample 3	1	9.38	17.25

References:

- (1) Rusanov, A. L.; Berlin, A. M.; Fidler, S. K.; Adyrkhaeva, F. I. Synthesis and Study of Some Bis(1',8'-Naphthoylene-1,2-Benzimidazoles). *Chem. Heterocycl. Compd.* 1979, 15 (7), 791–794.
- (2) Mizuguchi, J. Crystal Structure and Electronic Characterization of Trans- and Cis-Perinone Pigments. *J. Phys. Chem. B* 2004, 108 (26), 8926–8930.