

## ***Supporting Information***

### **Distinct Excited-State Dynamics of Near-Orthogonal Perylenimide Dimer: Conformational Planarization *versus* Symmetry Breaking Charge Transfer**

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## S1. Materials and experimental methods.

The synthesis and purification of **P**, **PP** were reported previously.<sup>1,2</sup> All solvents, including CHX, ACN, were of analytical grade and used as received. Steady-state UV/vis absorption spectra were recorded on a U-3010 (Hitachi) spectrophotometer. Steady state fluorescence spectra were recorded on an F-4600 (Hitachi) fluorescence spectrometer. Transient absorption measurements with a time resolution of  $\sim 90$  fs were performed by using a homemade femtosecond broadband pump-probe setup. Briefly, a regeneratively amplified Ti:sapphire laser (Coherent Legend Elite) produced 40 fs, 500 Hz repetition rate, 1 mJ pulses at  $\sim 800$  nm (FWHM: 30 nm). Doubling 90 percent of initial 800nm pulses through a 0.5 mm thick BBO (type I) crystal generated the 400 nm pump pulse and then this pulse pump an optical parametric amplifier (TOPAS-C, Light Conversion) to prepare the final pump pulse centered at 480 nm (60 fs). The rest of the 800 nm pulse was time-delayed by a computer-controlled optical delay line and then focused onto a 2 mm-thick water cell to produce a white light continuum (WLC), which provides a usable probe spectral range between 420 nm and 950 nm selected by a bandpass filter. The white light continuum was further split into two beams as the reference and signal beams by a broadband 50/50 beamsplitter. The pump and signal beams were overlapped in time and space on a sample cell with a 1 mm beam path length, and the reference beam passed through the unexcited part of the sample. The pump power is about 70 nJ/pulse (spot size of  $\sim 120 \mu\text{m}$  in each case) during transient absorption measurements. Signal and reference beams were detected on a fiber-coupled dual-channel spectrometer (Avantes AvaSpec-2048-2-USB2).

The collected time-dependent differential absorbance  $D(t, \lambda)$  was fitted by global

analysis using R-package TIMP software with the graphical interface Glotaran.<sup>3,4</sup>

Construction of a rational model describing the population kinetics of the transient species, is critical for global analysis of transient absorption data.

## S2. Additional femtosecond transient absorption spectra and kinetics of selected wavelengths of **P**.

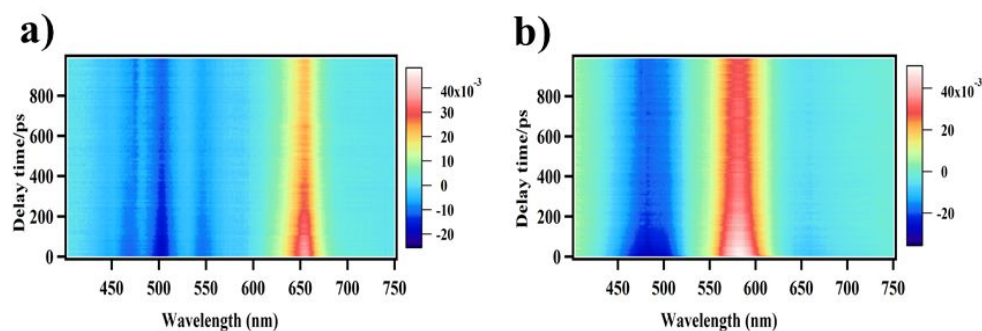


Figure S1. Transient absorption data of **P** map between 0 ps and 980 ps with pump at 480 nm in CHX (a) and ACN (b).

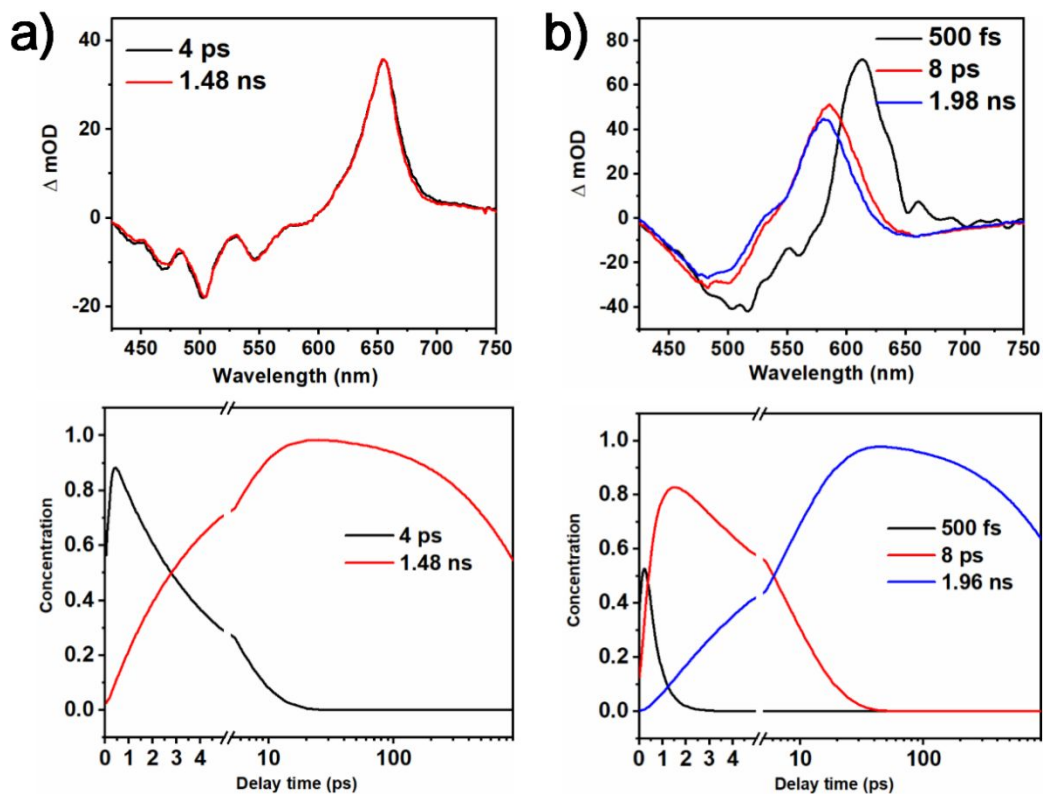


Figure S2. EADSs and the associated population evolution curves of the EADS components for monomer **P** in CHX (a) and ACN (b).

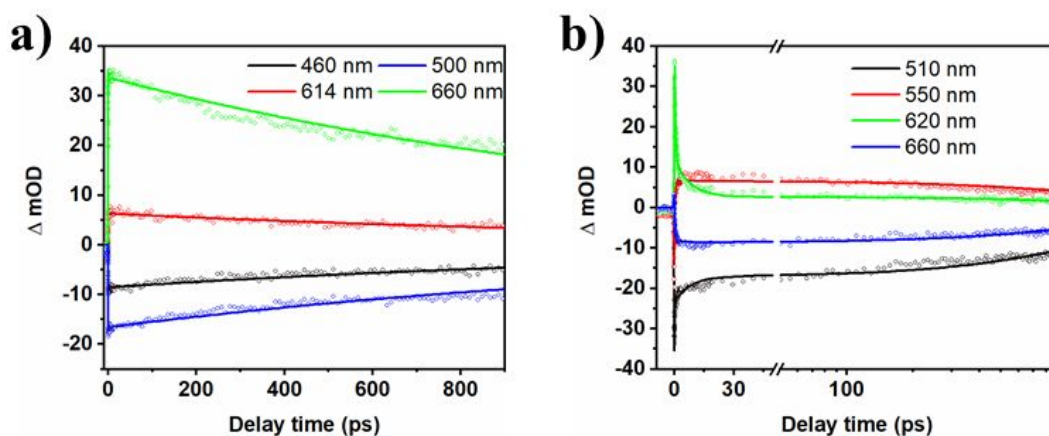


Figure S3. Plots of selected kinetic traces superimposed with matching curves at different wavelengths for **P** in CHX (a) and ACN (b).

**S3.** Additional femtosecond transient absorption spectra and kinetics of selected wavelengths of **PP**.

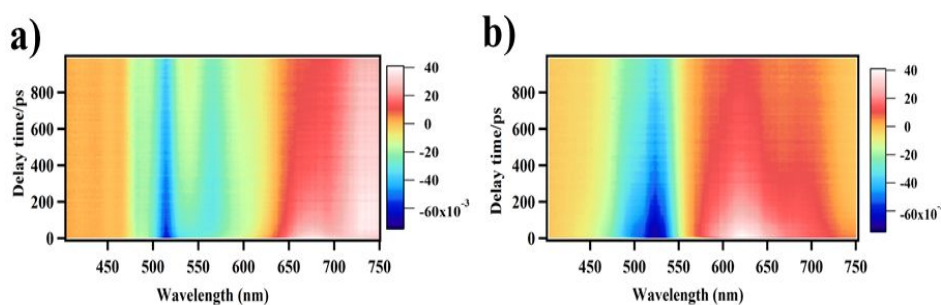


Figure S4. Transient absorption data of **PP** map between 0 ps and 980 ps with pump at 480 nm in CHX (a) and ACN (b).

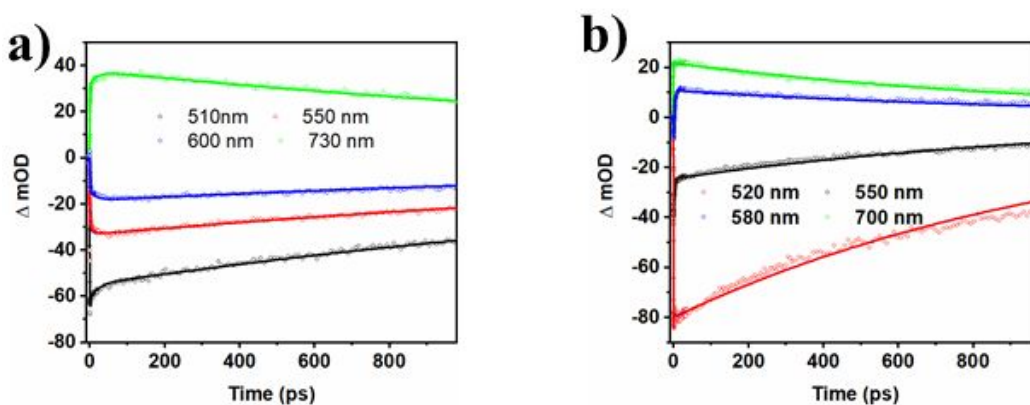


Figure S5. Plots of selected kinetic traces superimposed with matching curves at different wavelengths for **PP** in CHX (a) and ACN (b).

#### S4. Additional TD-DFT calculation results.

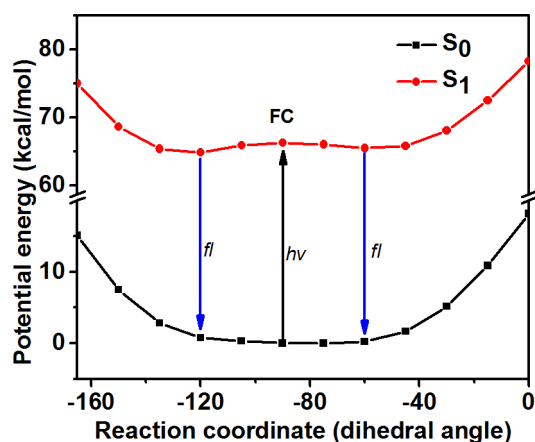


Figure S6. Energy profiles of ground state and excited state for **PP** along with the dihedral angle between two monomers.

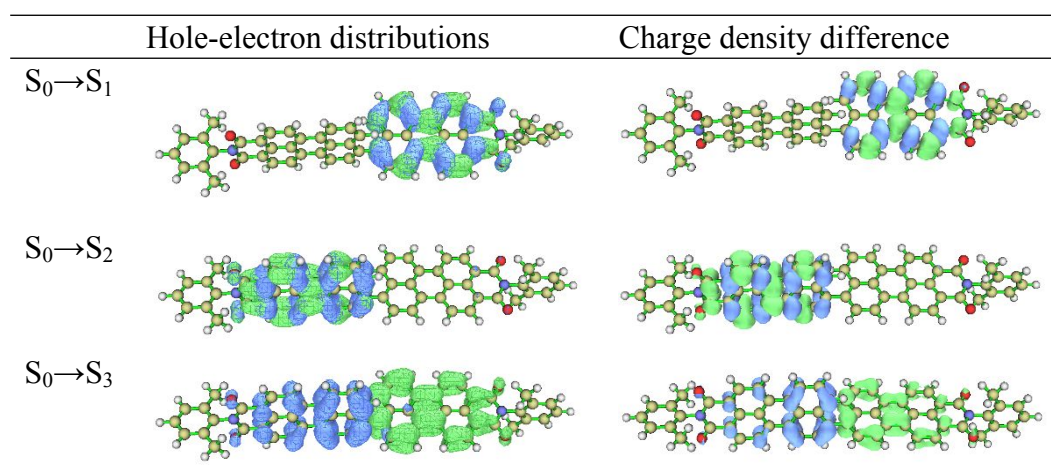


Figure S7. Distributions of hole and electron wave functions of  $S_1$ ,  $S_2$ ,  $S_3$  states and charge density difference for **PP** at optimized ground-state geometry in gas phase. The green and blue represent the electron and hole distributions, respectively.

Distributions of hole and electron wave functions of  $S_1$  and  $S_2$  can be used to examine the nature of  $S_0 \rightarrow S_1$  transition and  $S_0 \rightarrow S_2$  transition, suggesting that the first two singlet excited states belong to local excitation state from the left and right monomers, respectively. The slight overlap of the electron and hole distributions of  $S_3$  states at optimized ground geometry, in combination with calculated transition properties, indicate that the  $S_0 \rightarrow S_3$  is attributed to the ICT transition state.

## References

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