

Effect of Temperature on Symmetry Breaking Excited State Charge Separation: Restoration of Symmetry at Elevated Temperature

Hitesh Khandelwal, Ajith R. Mallia, Rijo T. Cheriya and Mahesh Hariharan*

^aSchool of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), CET Campus, Sreekaryam, Thiruvananthapuram, Kerala 695 016, Fax: (91)-471-2597427

Supporting Information Available

S. No.	Content	Page
1	Materials and method	2-3
2	Experimental section: Fig. S1 Shows the synthesis scheme of PP	4
3	Fig. S2 Electron density distributions and energies of frontier molecular orbital of PP	5
4	Fig. S3 Fluorescence life time of P and PP in various solvents	5
5	Fig. S4 Fluorescence lifetime decay profile of PP in acetonitrile (B) Arrhenius type plot for the nonradiative decay of PP in acetonitrile	6

Materials and Methods:

All chemicals were obtained from commercial suppliers and used as received without further purification. All reactions were carried out in glassware oven-dried prior to use and wherever necessary, were performed under dry nitrogen in dried, anhydrous solvents using standard gastight syringes, cannulae, and septa. Solvents were dried and distilled by standard procedures. TLC analyses were performed on precoated aluminum plates of silica gel 60 F254 plates (0.25 mm, Merck) and developed TLC plates were visualized under short and long wavelength UV lamps. Flash column chromatography was performed using silica gel of 200-400 mesh employing a solvent polarity correlated with the TLC mobility observed for the substance of interest. Yields refer to chromatographically and spectroscopically homogenous substances.

Melting points were obtained using a capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR spectrometer as neat thin films between NaCl plates in case of liquids and as KBr pellets in the case of solids. ^1H and ^{13}C NMR spectra were measured on a 500 MHz Bruker advanced DPX spectrometer. Internal standard used for ^1H and ^{13}C NMR is 1,1,1,1-tetramethyl silane (TMS). All CHN analyses were carried out on an Elementar vario MICRO cube Elemental Analyzer. All values recorded in elemental analyses are given in percentages. Absorption and emission spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR and Horiba Jobin Yvon Fluorolog spectrometers respectively. The fluorescence quantum yields were determined by using optically matched solutions. Nile red in dioxane ($\Phi_{\text{F}} = 0.7$)¹ were used as the standards for P and PP. Fluorescence lifetime measurements were carried out in an IBH picosecond single photon counting system. The fluorescence decay profiles were de-convoluted using IBH data station software version 2.1, and fitted with a mono-exponential and biexponential decay, minimizing the χ^2 values of the fit to 1 ± 0.05 . Laser flash photolysis experiments of the argon purged solutions were carried out in an Applied Photophysics Model LKS-60 laser kinetic spectrometer using the third harmonic (355 nm) of a Quanta Ray INDI-40-10 series pulsed Nd:YAG laser. Cyclic voltammetry was performed on a BASi E2 cyclic voltammeter with tetra butyl ammonium hexafluoro phosphate as supporting electrolyte in acetonitrile/chloroform mixture. A standard three-electrode configuration was used with a platinum disc (diameter: 1.6 mm) working electrode, a platinum wire auxiliary electrode and Ag/AgCl (3M NaCl) reference electrode. A scan rate of 100 mV/s was used throughout the measurements. The scans were performed using a Ag/AgCl reference electrode with a ferrocene-ferrocenium couple (Fc/Fc^+) as an external standard (+0.47 V vs Ag/AgCl in CH_3CN). Electrochemical measurements were performed at room temperature with nitrogen-purged solutions.

UV-Vis spectroelectrochemical studies were carried out using Ocean Optics DT-Mini-2 UV-Vis spectrometer coupled with the BASi E2 cyclic voltammeter. All spectroscopic experiments were performed using standard quartz cuvettes of path length 1 cm and using dried and distilled solvents.

Computational methods: DFT geometry optimization using nonlocal hybrid three-parameter Lee-Yang-Parr (B3LYP) level of theory with the (6-31G) basis set as implemented in the Gaussian 09W program suite was performed to optimize all the structures and energy of the frontier molecular orbitals (FMO) was obtained using simple extended Hückel approximation using ChemBioOffice Ultra 2010. Output of the calculations was viewed and analysed using GaussView 5.0.

Femtosecond Transient absorption spectroscopy: Spectra-physics Tsunami Oscillator (80 MHz, 800 nm) was used as seed for a Spectra-Physics Spitfire Regenerative amplifier (1 KHz, 4 mJ). A fraction of the amplified output was used to generate 400 nm pump pulse. Residual 800 nm pulse was sent through a delay line inside the ExciPro pump-probe spectrometer from CDP Systems. A rotating CaF₂ plate (2 mm thickness) was used to generate white light continuum from the delayed 800 nm pulses. The white light continuum was split into two and was used as probe and reference pulses. Transient absorption spectra were recorded using a dual Diode array detector with a 200 nm detection window. Sample solutions were contained in a rotating sample cell with 400 μ m path length. IRF was determined by solvent (10% Benzene in Methanol) two photon absorption and was found to be approximately 130 fs at about 530 nm.

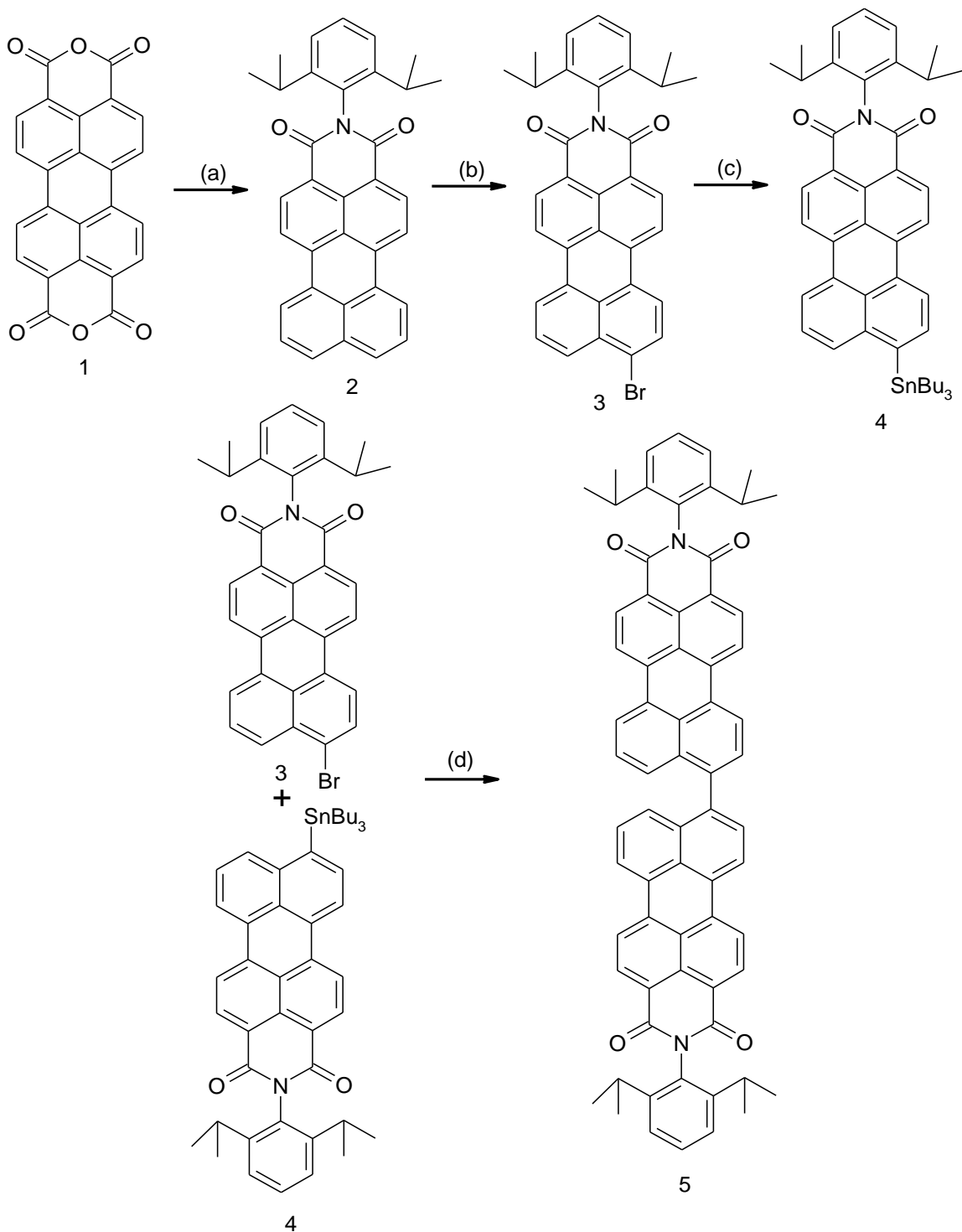


Fig. S1 Shows the synthesis scheme of N,N'-Bis(2,6-diisopropylphenyl)-9,9'-biperylene-3,4:3',4'-bis(dicarboxyimide). (a) 2,6-diisopropylaniline, zinc acetate, imidazole, H₂O, 190 °C, 23 hrs (b) chlorobenzene, Br₂, 50 °C, 4.5 hrs (c) hexabutyltin, Pd(PPh₃)₄, Toluene, reflux, 72 hrs (d) DMF, Pd(PPh₃)₄, reflux, 72 hrs.

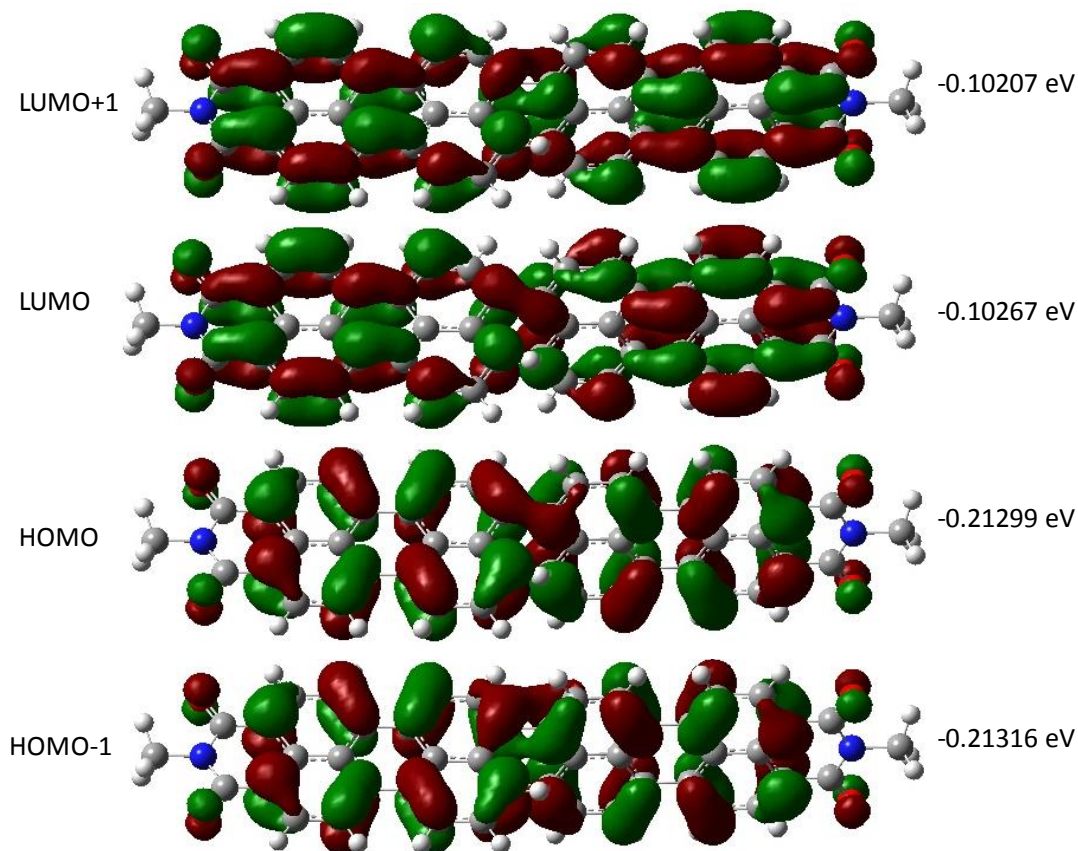


Fig. S2 Electron density distributions and energy of frontier molecular orbitals (FMO) of **PP**.

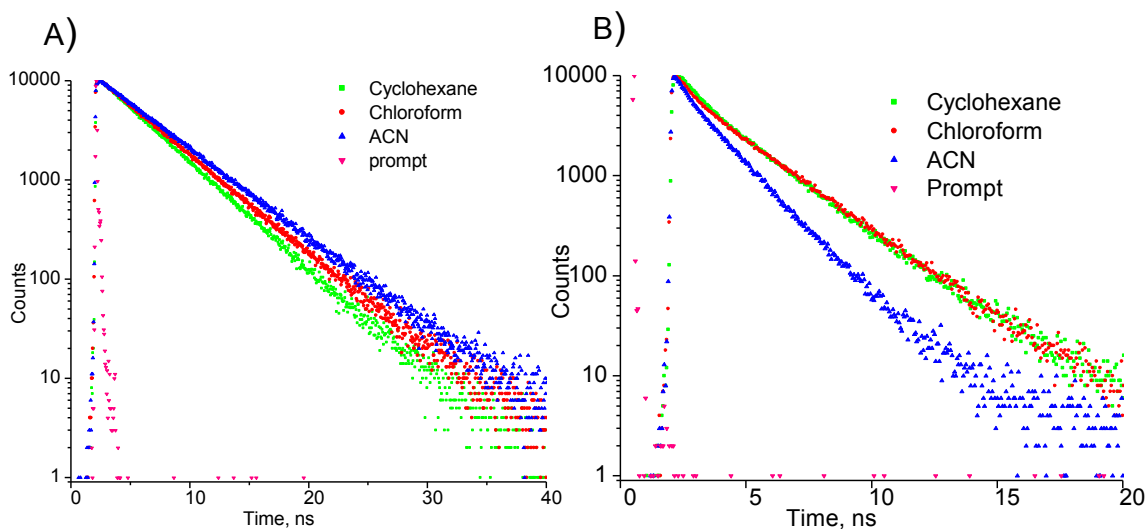


Fig. S3 Fluorescence life time excited at 439 nm of (A) **P** and collected at 509, 540 and 545 nm in cyclohexane chloroform and ACN respectively (B) **PP** and collected at 564, 598 and 635 nm cyclohexane, chloroform and ACN respectively.

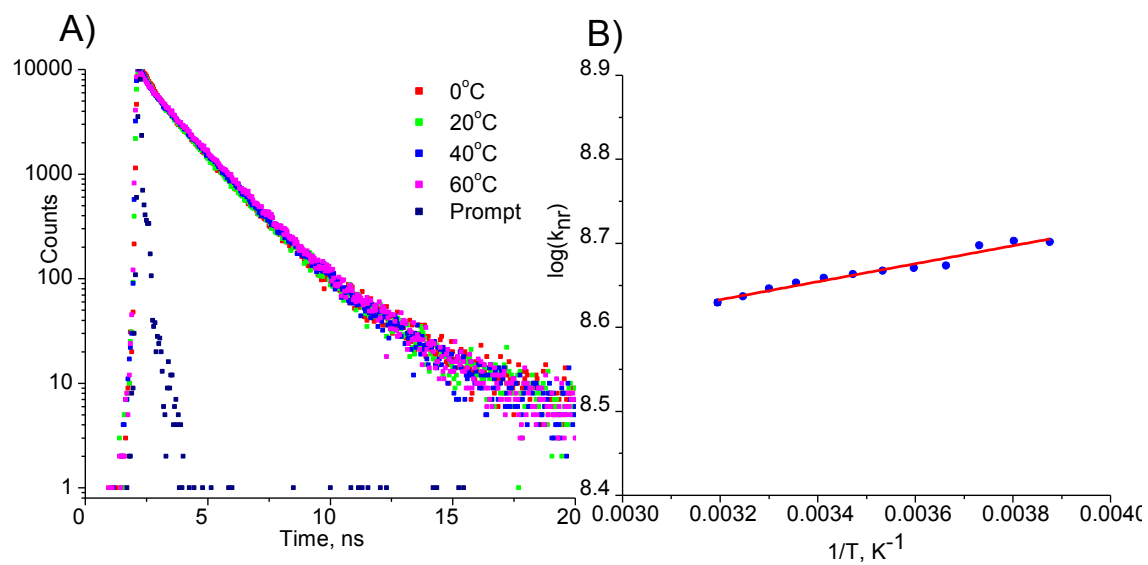


Fig. S4 Fluorescence lifetime decay profile of dimeric **PP** in acetonitrile at various temperature (0 to 70 °C); excited at 439 nm and emission collected at 635 nm; (B) Arrhenius type plot for the nonradiative decay of dimeric **PP** in acetonitrile.