Supporting Information

Exciton delocalization and dynamics in helical π-stacks of self-assembled perylene bisimides

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EXPERIMENTAL METHODS

Sample preparation Tetracarboxylic acid bisimide (PBI) dyes **1**, **2**, **3**, and **4** were synthesized according to previously reported procedures.[1-3] In all spectroscopic experiments, chloroform and methylcyclohexane were used as solvent (Sigma-Aldrich, spectrophotometric grade) without further purification. For quencher embedment experiments, standard solution of PBI dyes **1** and **4** are prepared in chloroform solvent. After mixing two standard solutions of PBI **1** and **4** with proper ratios (1000, 100, 10, and 5 versus 1), chloroform solvent was evaporated and the hetero-PBI dyes were dissolved in methylcyclohexane solvent. By using this solution of hetero-PBI dyes, we have examined the fluorescence spectra and the pump-power dependency in fs-transient absorption measurements.

Steady-state absorption and fluorescence measurements UV-vis spectra were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer and fluorescence spectra were recorded with a Hitachi model F-2500 fluorescence spectrophotometer.

Fluorescence lifetime and time-resolved fluorescence anisotropy A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay and fluorescence anisotropy decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). This high repetition rate slows down to 1M ~ 800 kHz by using homemade pulse-picker. The pulse-picked output pulse was frequency-doubled by a 1 mm thickness of a BBO crystal (EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker&Hickel SPC-130). The overall instrumental response function was about 25 ps (fwhm). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Femtosecond transient absorption measurement Femtosecond (fs) time-resolved transient absorption (TA) spectra were recorded using a spectrometer consisting of a homemade noncollinear optical parametric amplifier (NOPA) pumped by a Ti:sapphire regenerative amplifier system

(Quantronix, Integra-C) operating at 1 kHz repetition rate coupled with an optical detection system. The generated visible NOPA pulses had a pulse width of ~ 100 fs and an average power of 1 mW in the range 480-700 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses that were picked off by a quartz plate before entering into the NOPA. The time delay between pump and probe beams was carefully controlled by causing the pump beam to travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses are monitored by a miniature spectrograph (OceanOptics USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and the absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses were used to excite the samples so as to obtain a TA spectra at a particular delay time. The polarization angle between the pump and probe beams was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder so as to prevent polarization-dependent signals. The cross-correlation fwhm in the pump-probe experiments was less than 200 fs and the chirp of WLC probe pulses was measured to be 800 fs in the 400-1250 nm region. To minimize chirp, all-reflection optics in the probe beam path and a 2 mm path length quartz cell were used. After the TA experiments, the absorption spectra of all compounds was carefully checked so as to avoid artifacts arising from, e.g., photo-degradation or photo-oxidation of the samples in question. HPLC grade solvents were used in all steady-state and time-resolved spectroscopic studies.

Femtosecond transient absorption anisotropy decay Dual-beam femtosecond time-resolved transient absorption (TA) spectrometer consisted of two independently-tunable home-made noncollinear optical parametric amplifiers (NOPA) pumped by a regeneratively amplified Ti:sapphire laser system (Spectra-Physics, Hurricane-X) operating at 3 kHz repetition rate and an optical detection system. The NOPA was based on non-collinearly phase-matching geometry, which was easily color-tuned by controlling optical delay between white light continuum seed pulses (450-1400 nm) and visible pump pulses (400 nm) produced by using a sapphire window and BBO crystal, respectively. The generated

visible OPA pulses had a pulse width of ~ 35 fs and an average power of 10 mW at 3 kHz repetition rate in the range 500-700 nm after a fused-silica prism compressor. Two OPA pulses were used as the pump and probe pulses, respectively, for TA measurement. The probe beam was split into two parts. The one part of the probe beam was overlapped with the pump beam at the sample to monitor the transient (signal), while the other part of the probe beam was passed through the sample without overlapping the pump beam to compensate the fluctuation of probe beam. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). To obtain the time-resolved transient absorption difference signal at specific wavelength, the monitoring wavelength was selected by using a narrow interference filter (FWHM ~10 nm). By chopping the pump pulses at 47 Hz, the modulated probe pulses as well as the reference pulses were detected by two separate photodiodes (New Focus, Femtowatt Photoreceiver). The modulated signals of the probe pulses were measured by a gated-integrator (SRS, SR250) and a lock-in amplifier (EG&G, DSP7265) and stored in a personal computer for further signal processing. In general experimental conditions, time-resolutions of less than 50 fs were achieved. For anisotropy measurement, both $I_{\parallel}$ and $I_{\perp}$ signals were collected simultaneously by combination of polarizing beam-splitter cube and dual lock-in amplifiers as following equation:[4]

$$r(t) = (I_{\parallel} - I_{\perp}) / ((I_{\parallel} + 2I_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ represent TA signals with the polarization of the pump and probe pulses being mutually parallel and perpendicular respectively. The pump pulse was set to vertical polarization and that of probe pulse was set to 45° with respect to the pump pulse by using Glan-laser polarizers and half-wave plates. After the probe pulse passes through the sample cell, it was split by a polarizing beam-splitter cube and then detected by two separate photodiodes. Two gated-integrators and two lock-in amplifiers record the signal simultaneously within a single scan. As a standard anisotropy measurement showed a clean single exponential decay with reorientational relaxation times of 122.1 ± 0.3 ps and the initial anisotropy $r_{(0)}$ value of 0.39 ± 0.02 for rhodamine 6G dye in methanol, which are well-matched in other reference.[5] For all TAA measurements, wavelength of pump and probe pulses were set to 550 nm

with an average power of less than 40 μW and 690 nm, respectively. A thin absorption cell with a pathlength of 500 μm was used to eliminate additional chirping.

Fluorescence up-conversion spectroscopy A femtosecond fluorescence up-conversion apparatus was used for the time-resolved spontaneous fluorescence. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). The second harmonic of the fundamental generated by a 200-μm thick BBO crystal served as pump pulse. Residual fundamental pulse was used as a gate pulse. The pump beam was focused onto a 500-μm thick quartz cuvette containing sample solution using a 5-cm focal length plano-convex lens with a magic angle (54.7°) in order to prevent polarization-dependent signals. The cuvette was mounted on a motor-driven stage and moved constantly back and forth to minimize photo-degradation. Collection of the fluorescence and focusing into a 500 μmm-thick BBO crystal for frequency conversion was achieved by a reflecting microscope objective lens (Coherent). The FWHM of the cross-correlation function between the scattered pump pulse and the gate pulse is measured to be ~340 fs. The average excitation power was kept at a level below 2 mW in order to minimize thermal lens effect. In this excitation intensity regime the fluorescence dynamics was be independent of the excitation intensity for all samples.

References

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2) Z. Chen, U. Baumeister, C. Tschierske and F. Würthner, *Chem. Eur. J,* 2007, **13**, 450-465.

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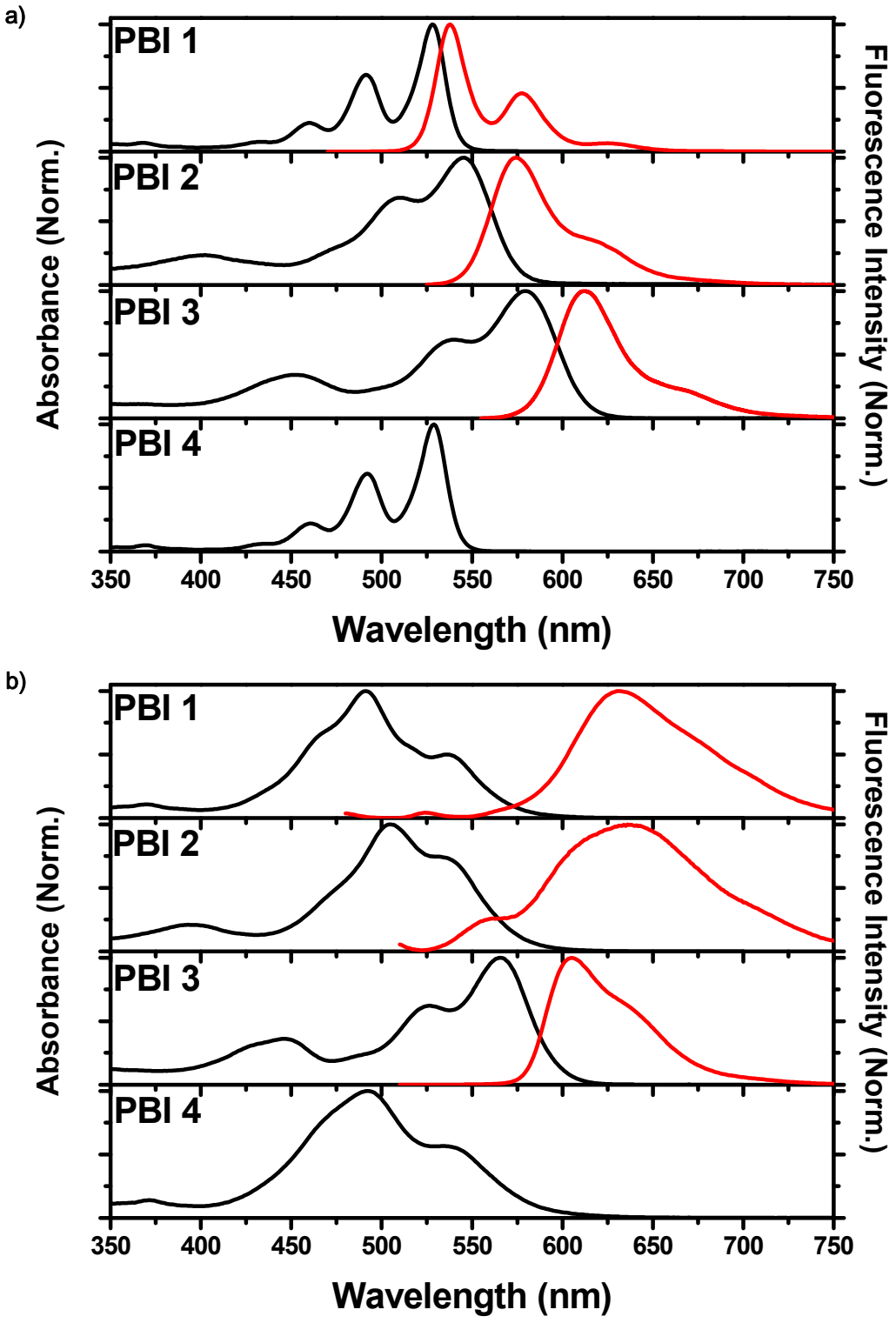
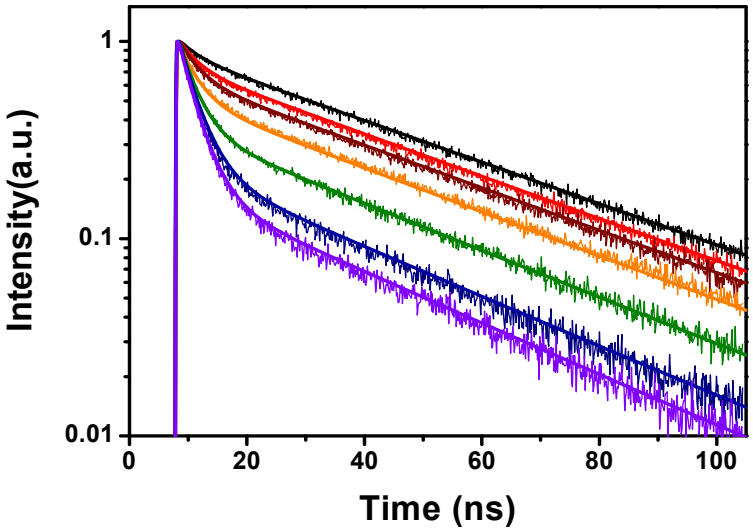


Fig. S1 Steady-state absorption spectra and fluorescence emission of PBI **1**, PBI **2**, PBI **3**, and PBI **4** in a) chloroform (~10^{-6} M) and b) methylcyclohexane (~10^{-3} M).



	τ_1	τ_2
10^{-5} M	**3.30** (17.3%)	**40.92** (82.7%)
$6.7*10^{-6}$ M	**3.21** (29.3%)	**40.25** (70.7%)
$5*10^{-6}$ M	**3.30** (38.0%)	**39.95** (62%)
$3.4*10^{-6}$ M	**3.18** (49.6%)	**38.69** (50.4%)
$2*10^{-6}$ M	**3.00** (67.2%)	**36.16** (32.8%)
$1.4*10^{-6}$ M	**3.23** (79.0%)	**34.03** (21.0%)
10^{-6} M	**3.08** (83.6%)	**32.91** (16.4%)

Fig. S2 Concentration dependent fluorescence decay profiles of PBI **1** in methylcyclohexane. The shorter time components are correspond to the PBI monomer and the longer ones represent the fluorescence lifetime of aggregates forms.

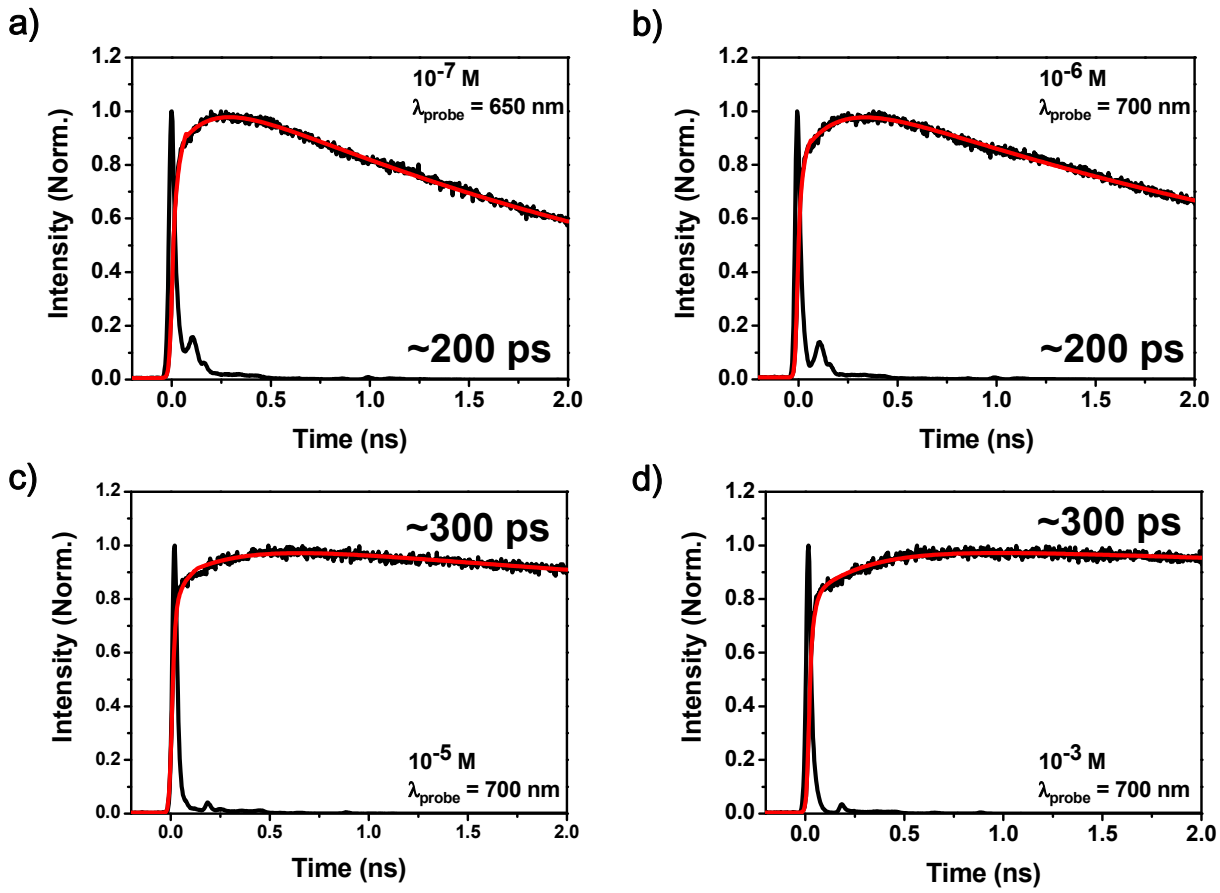


Fig. S3 Concentration dependent fluorescence rise and decay profiles of PBI **1** in methylcyclohexane. The excimer fluorescence emission signals are observed at 650 and 700 nm.

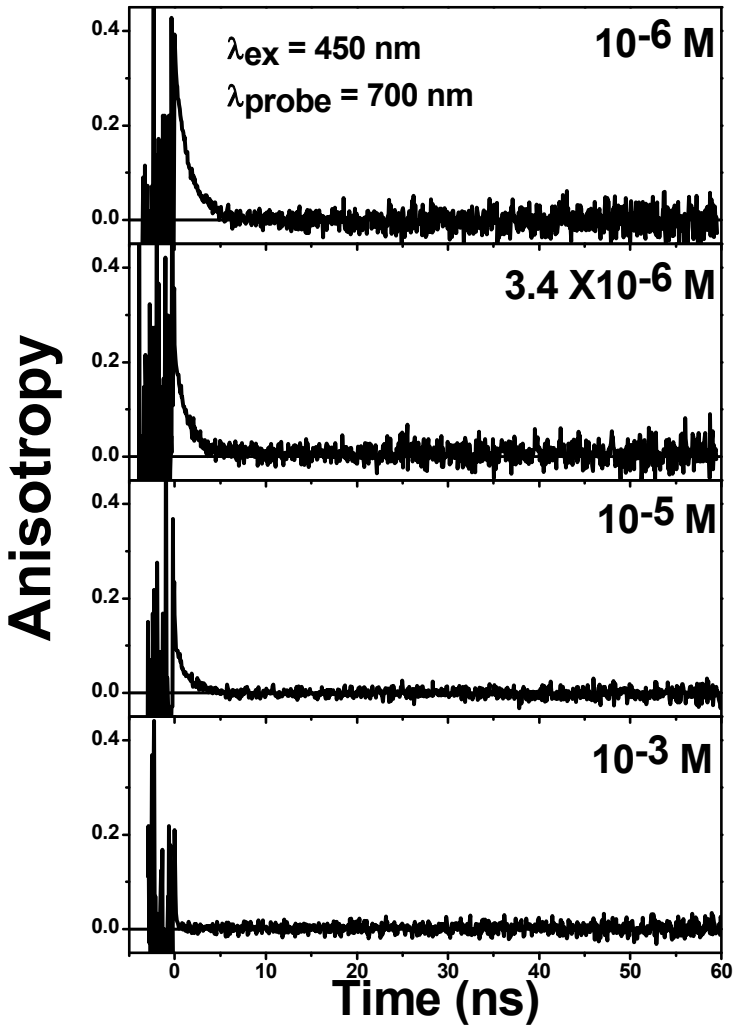


Fig. S4 Concentration dependent fluorescence anisotropy changes of PBI **1** in methylcyclohexane.

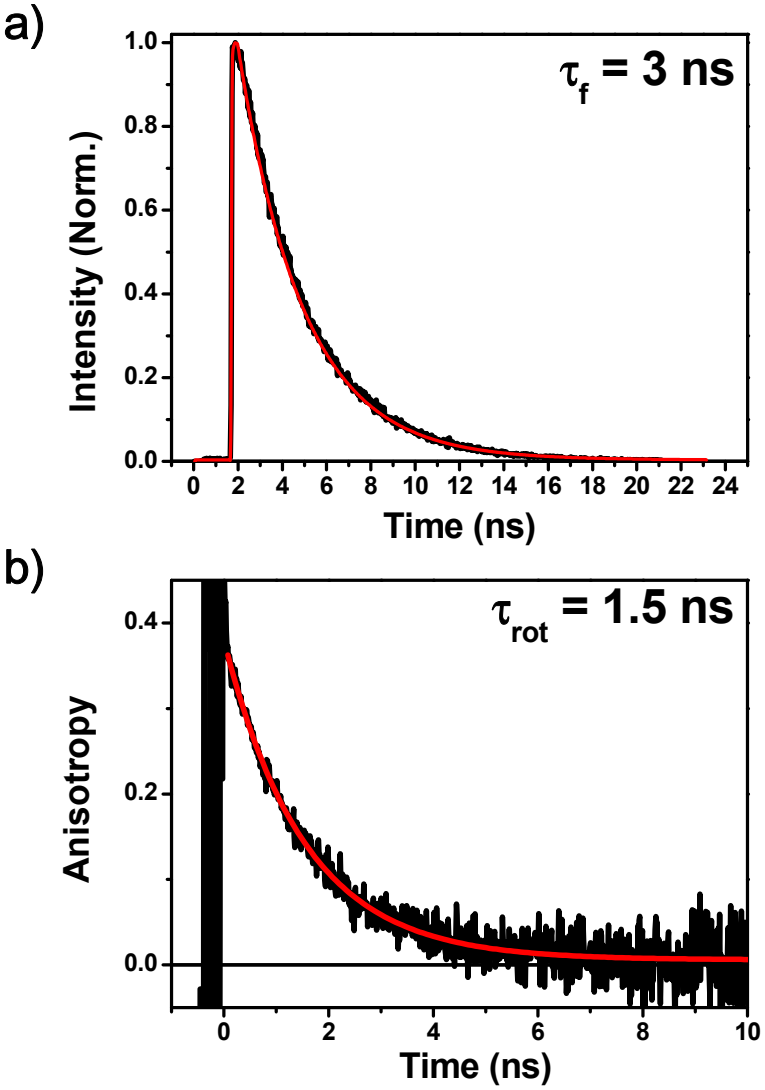


Fig. S5 Fluorescence (a) and anisotropy decay (b) profiles of PBI **1** (10^{-7} M) in methylcyclohexane. Fluorescence and anisotropy decay profiles are observed at 520 and 700 nm, respectively.

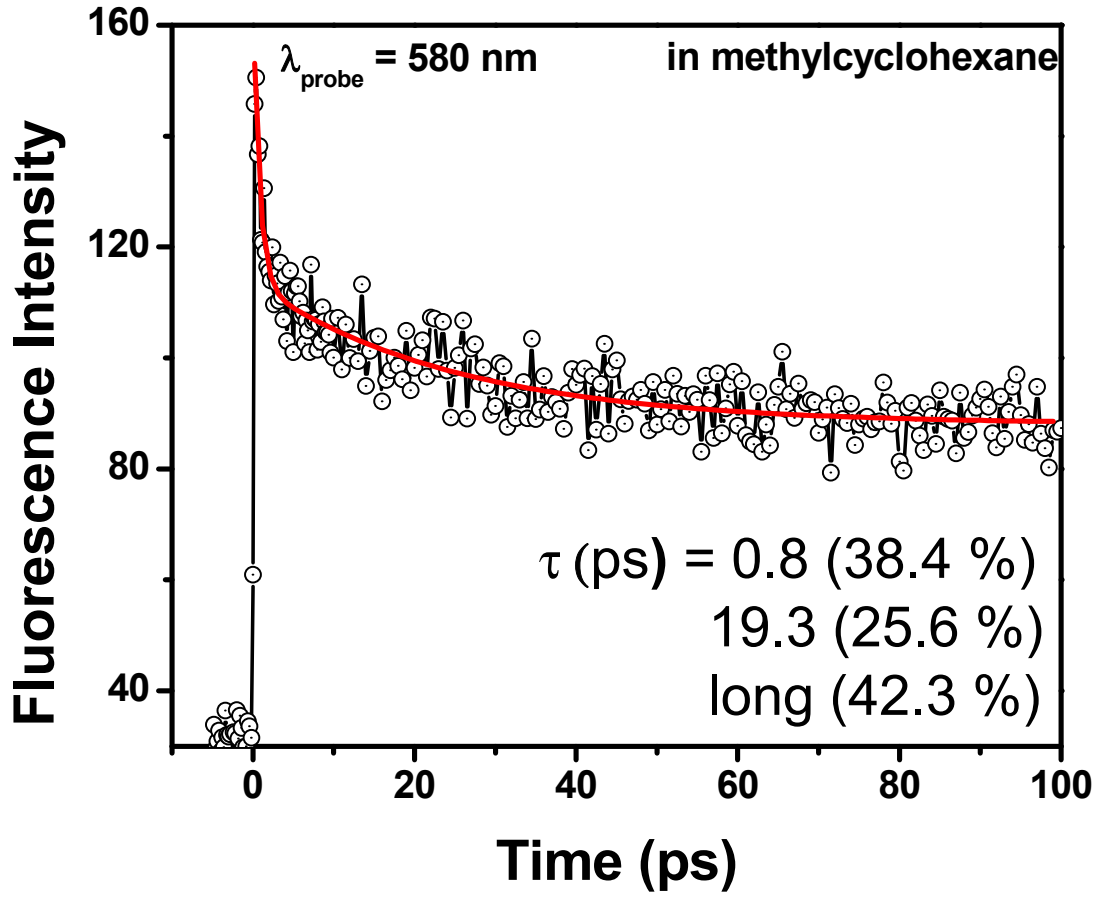


Fig. S6 Fluorescence decay profile of PBI **2** (10^{-3} M) at 580 nm.

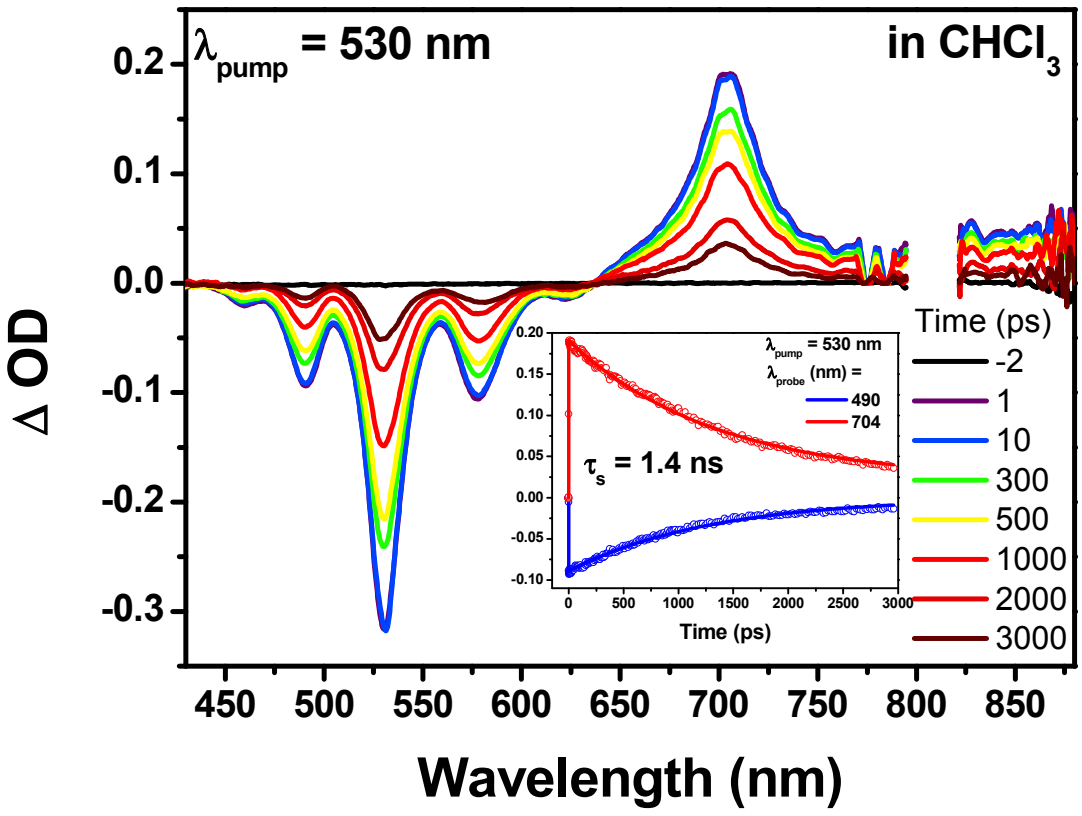


Fig. S7 Femtosecond transient absorption spectra and decay profiles (inest)of PBI **1** in chloroform.

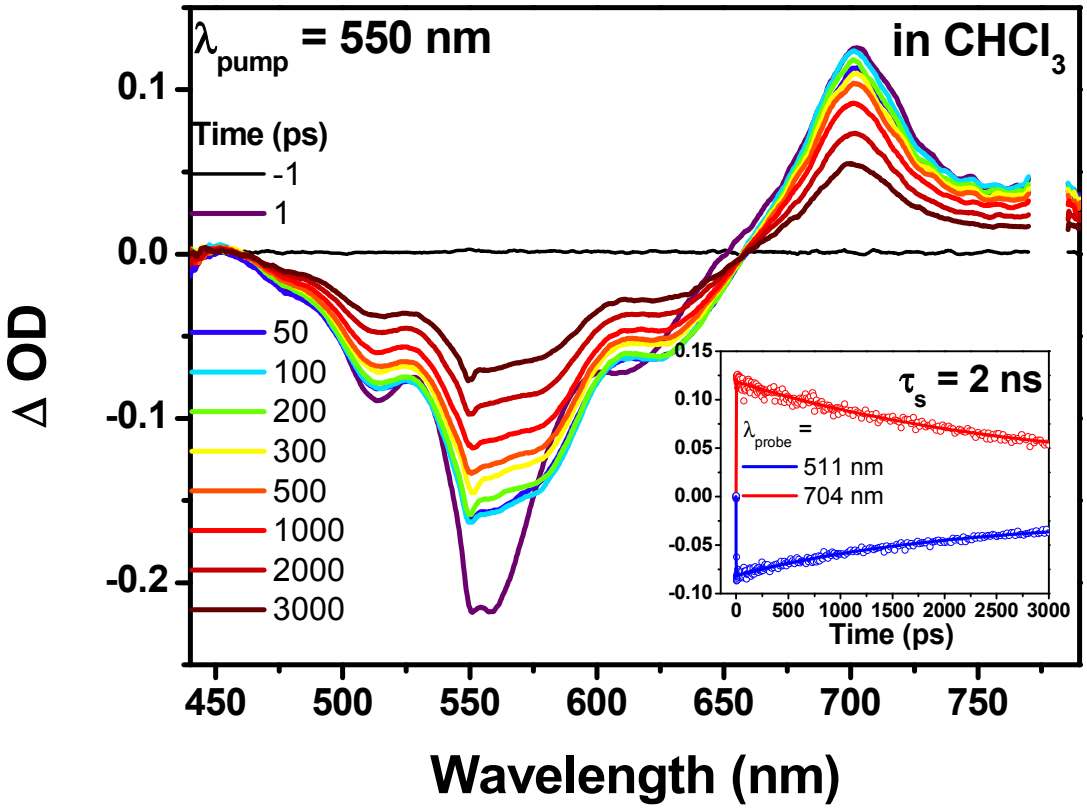


Fig. S8 Femtosecond transient absorption spectra and decay profiles (inest) of PBI **2** in chloroform. The time profile shows single exponential decay curve and the singlet excited-state lifetime is estimated to be 2 ns.

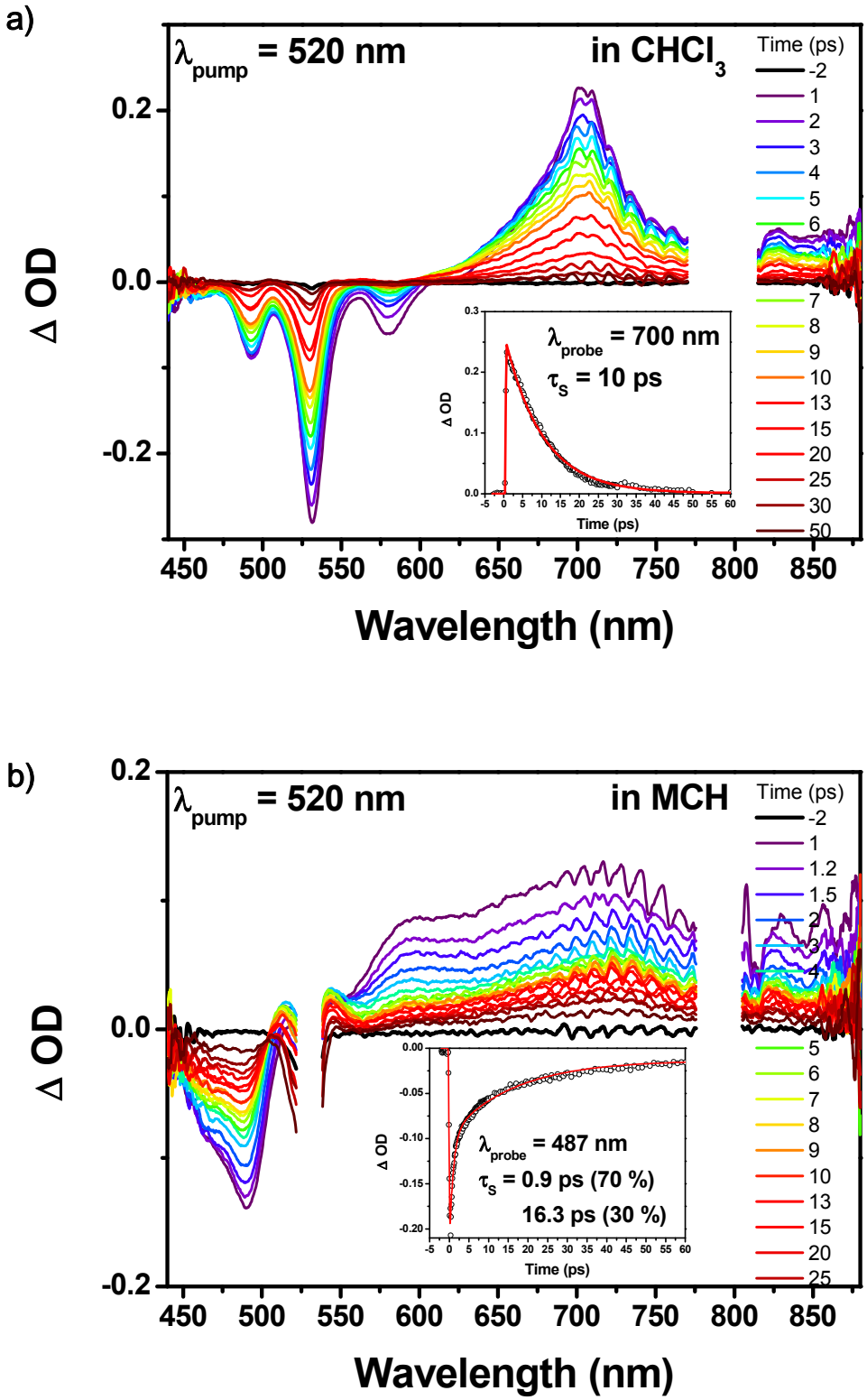


Fig. S9 Femtosecond transient absorption spectra and decay profile (inset) of PBI **4** in a) chloroform and b) methylcyclohexane.

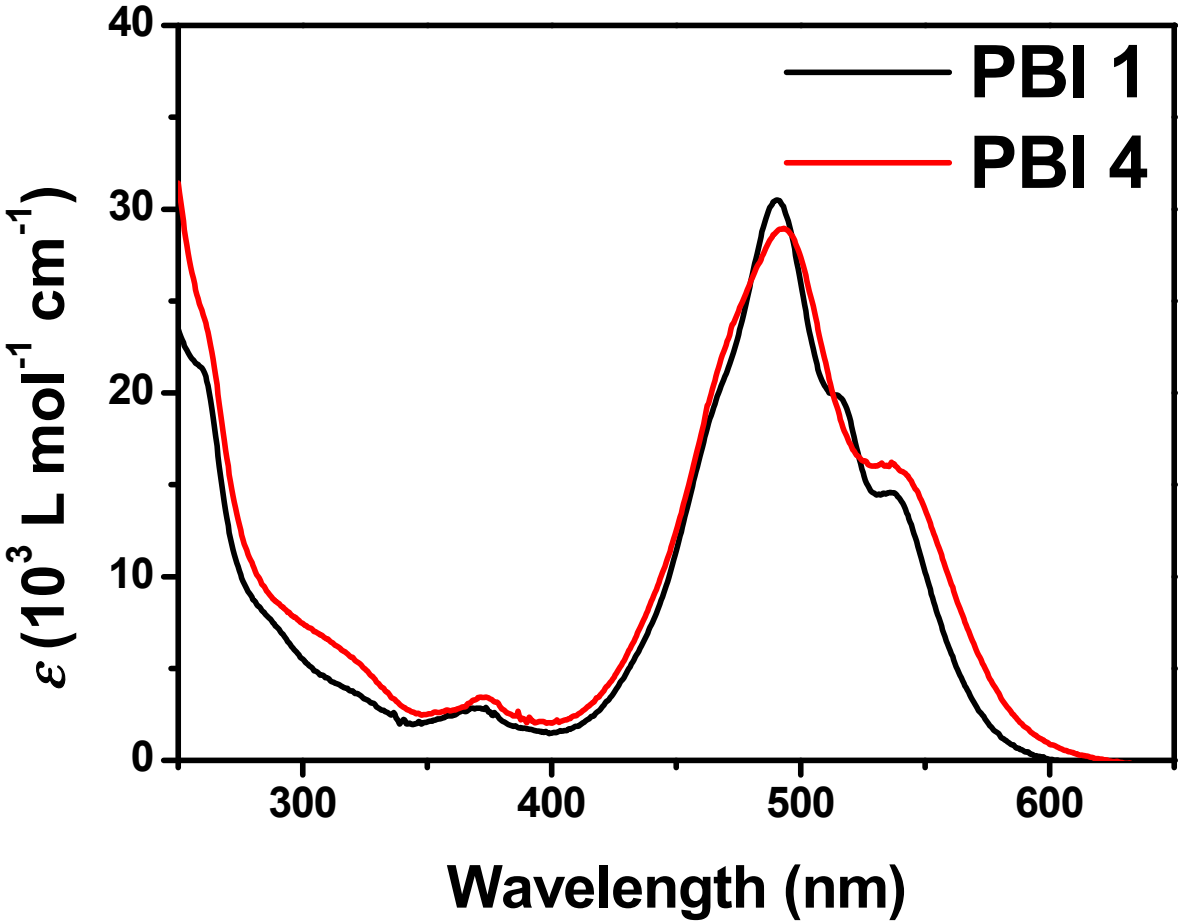


Fig. S10 Comparison of steady-state absorption spectra of PBI **1** (black, 1.3×10^{-4} M), and PBI **4** (red, 1.3×10^{-4} M) in methylcyclohexane.

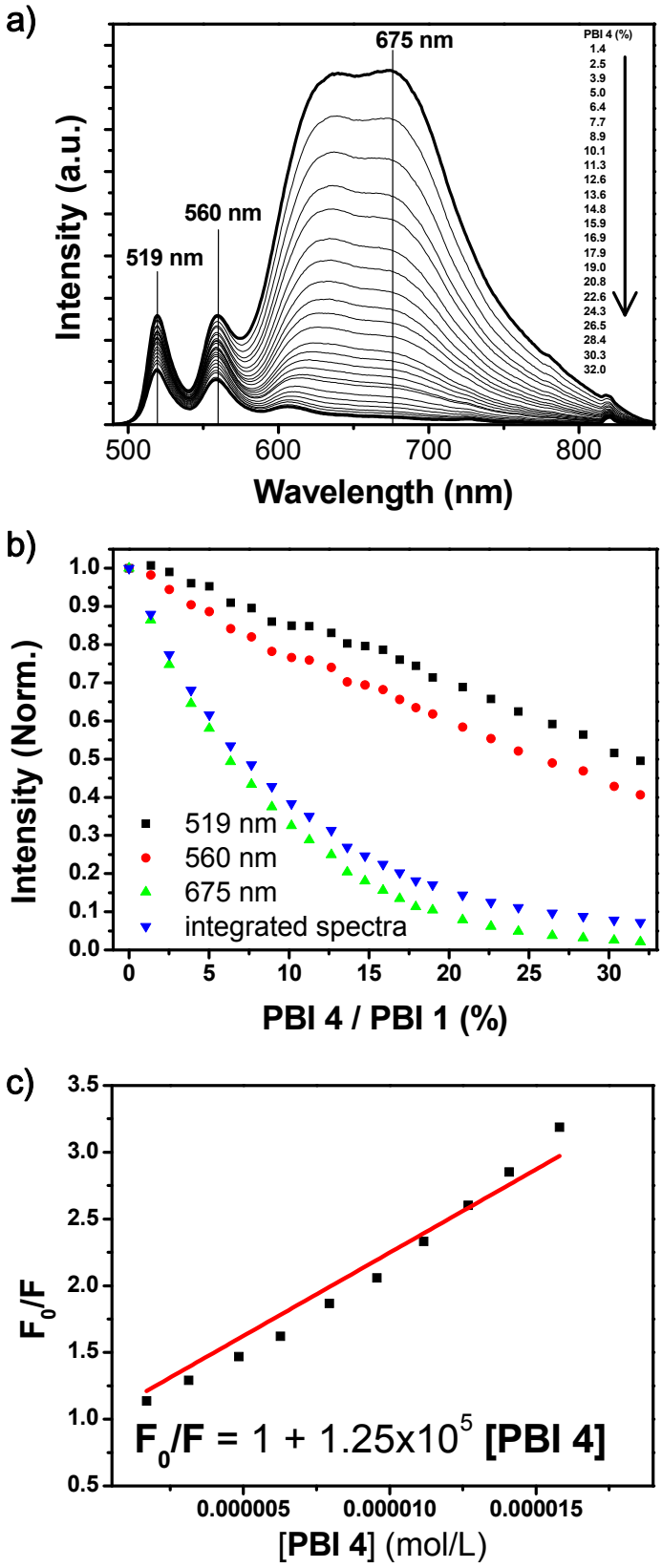


Fig. S11 Fluorescence a) spectral and its b) peak intensity change and c) Strem-Volmer plot for the hetero-aggregates PBI. Ratio PBI **4** / PBI **1** is controlled.

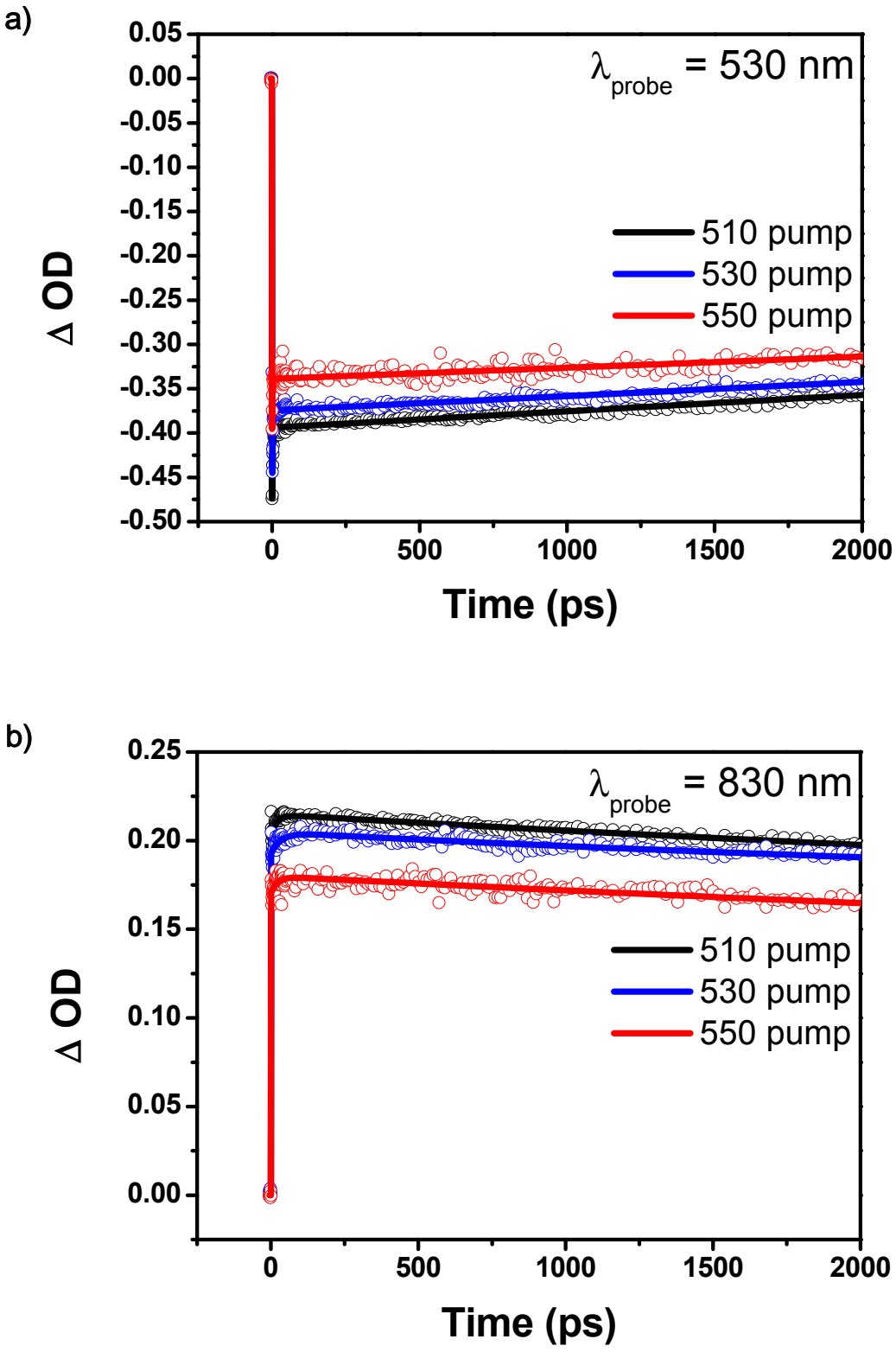


Fig. S12 Femtosecond transient decay profiles of PBI **1** (10^{-3} M) with various excitation wavelengths (510, 530 and 550 nm) in methylcyclohexane .