Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Energy transfer and spectroscopic characterization of perylenetetracarboxylic diimide (PDI) hexamer

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S1. Absorption spectra of PDI-hexamer at different concentrations

Figure S1 shows absorption spectra of PDI-hexamer dissolved in chloroform at different concentrations (1.0×10^{-5} M and 1.0×10^{-7} M). The same spectral shapes at different concentrations indicate that aggregation from different PDI-hexamers could be ignored.

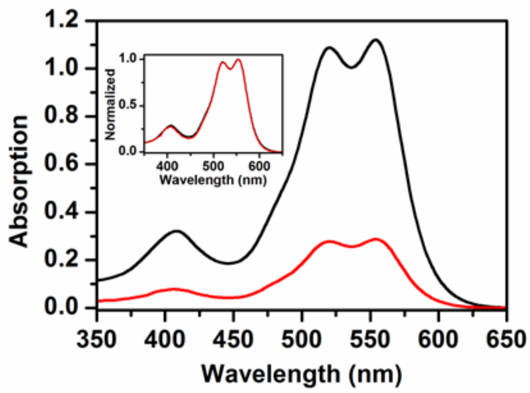

Figure S1. Absorption spectra of PDI-hexamer dissolved in chloroform at different concentrations. (black, 1.0×10^{-5} M, red, 1.0×10^{-7} M) Inset shows normalized absorption spectra of PDI-hexamer at different concentrations, which show no obvious differences.

S2. Fluorescence excitation spectra of PDI-monomer, -dimer and -hexamer monitored at different emission wavelengths

As shown in Figure S2, the fluorescence excitation spectra of PDI-monomer completely resemble the absorption spectrum of monomer, and there is no difference for the excitation spectra of monomer monitored at different emission wavelengths; Whereas, the fluorescence excitation spectra of PDI-dimer shows a little redshift compared to that of monomer, which may result from the weakly coupled two distant monomers within free PDI-dimer as shown in Figure S5a. More interestingly, the fluorescence excitation spectra of PDI-hexamer shows significant decrease of intensity ratios of $I_{555\ \mathrm{nm}}/I_{520\ \mathrm{nm}}$ when the monitored emission wavelength is changed from blue-side to red-side of emission spectra, suggesting the formation of the low-energy pre-associated excimer in ground state. This indicates that there is some level of pre-associated excimer formed already in the ground state because of steric effect for dimer in hexamer.

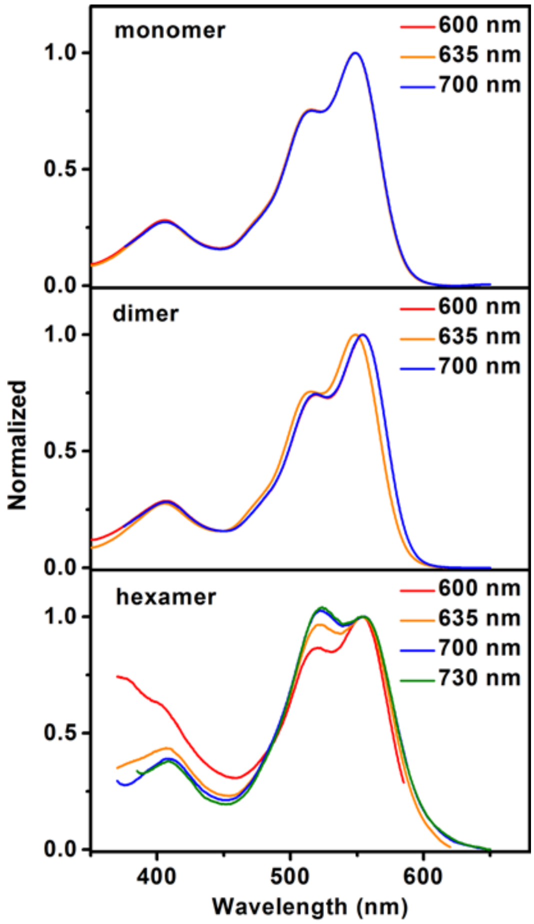

Figure S2. Normalized fluorescence excitation spectra of PDI-monomer, -dimer and -hexamer monitored at different emission wavelengths.

S3. Fluorescence lifetime measurements of PDI-monomer, -dimer and -hexamer by TCSPC

Figure S3 shows the measured fluorescence lifetimes of PDI-monomer and -dimer by time correlated single photon counting (TCSPC) measurements. It is found that the lifetimes of PDI-monomer monitored at different wavelengths are all about 4.8 ns, while that of PDI-dimer shows a little shorter about 3.3 ns relative to monomer. The shorter lifetime (~3.3 ns) of dimer may result from possibly weakly coupled J-type dimer as shown from energy-minimized structure of PDI-dimer in Figure S5a. The interaction between two monomers is so weak that the spectral features of free PDI-dimer is similar as that of PDI-monomer.

Meanwhile, the lifetime of PDI-hexamer shows two typical lifetimes with a short one about 3.3 ns and a long one about 20 ns (see Figure S4). The short lifetime (~3.3 ns) is corresponding to the interacted exciton state or monomer dominated at blue-side of emission spectra, and the long lifetime (~20 ns) mainly corresponds to the excimer state of PDI-hexamer. As shown in Table S1, the increasing pre-exponential factor of the long lifetime monitored at long emission wavelengths suggests the formation of typical low-energy excimer state in PDI-hexamer.

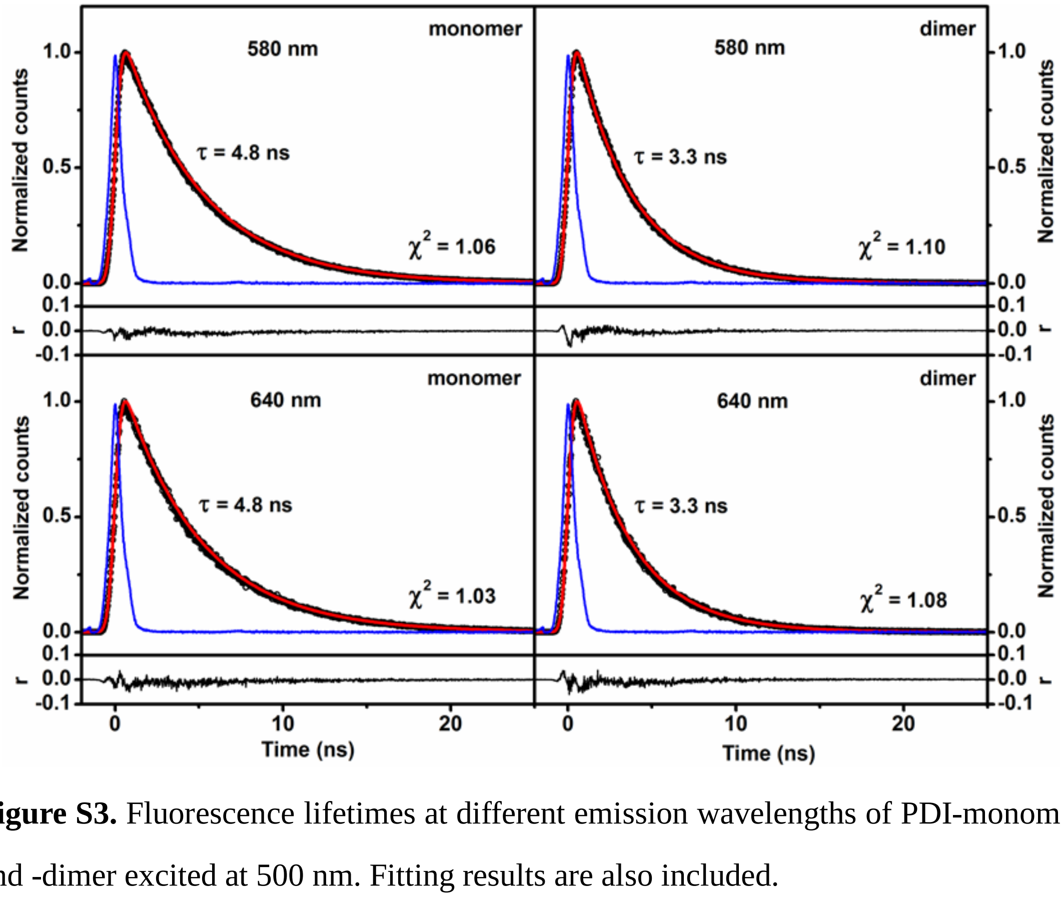

Figure S3. Fluorescence lifetimes at different emission wavelengths of PDI-monomer and -dimer excited at 500 nm. Fitting results are also included.

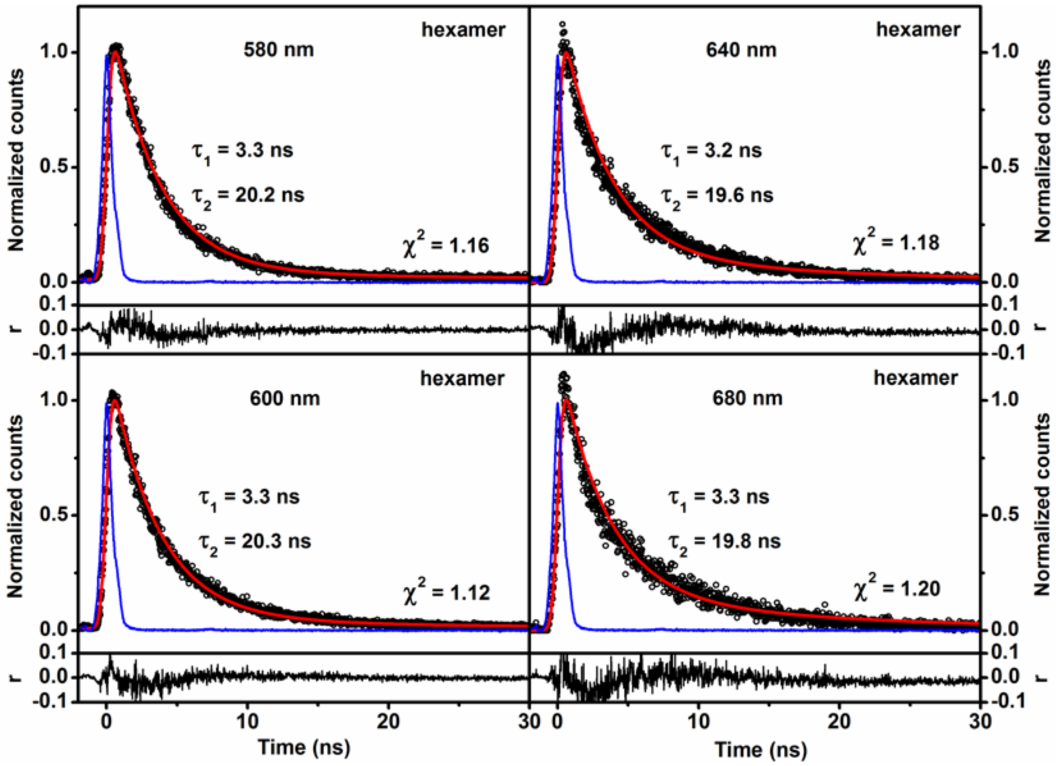

Figure S4. Fluorescence lifetimes at different emission wavelengths of PDI-hexamer excited at 500 nm. Fitting results are also included.

Table S1. Fitting parameters of PDI-hexamer fluorescence lifetimes at different emission wavelengths.

Emission wavelength	τ_1	τ_2
580 nm	3.3 ns (96.8%)	20.2 ns (3.2%)
600 nm	3.3 ns (94.0%)	20.3 ns (6.0%)
640 nm	3.2 ns (90.0%)	19.6 ns (10.0%)
680 nm	3.3 ns (86.0%)	19.8 ns (14.0%)

S4. Energy-minimized structure and transient absorption results of free PDI-dimer

In free dimer, two PDIs are distant from each other because of the flexible linker, and both the steady-state and transient absorption spectra behave more like two independent monomers as shown in Figure 1, Figure S5 and Table S2. It is believed that the geometrical arrangement of two PDI units in free dimer is totally different from that in hexamer because of the flexible linker in dimer. Figure S5a shows the optimized energy-minimized ground state structure of PDI-dimer and it is found that the rotational displacement angle is much larger in dimer (Ψ = 119°) totally different from that in hexamer (Ψ = 38°). In this case, the two PDIs in free dimer are distant from each other because of the flexible linker, and the steady-state spectra of free PDI-dimer (see Figure 1) behave more like two independent (or weak-coupled) monomers. Furthermore, the femtosecond transient absorption spectra for free PDI-dimer in chloroform following excitation at 400 nm and the fitted results based on sequential reaction scheme are all similar to that of PDI-monomer. (see Figure S5 and Table S2)

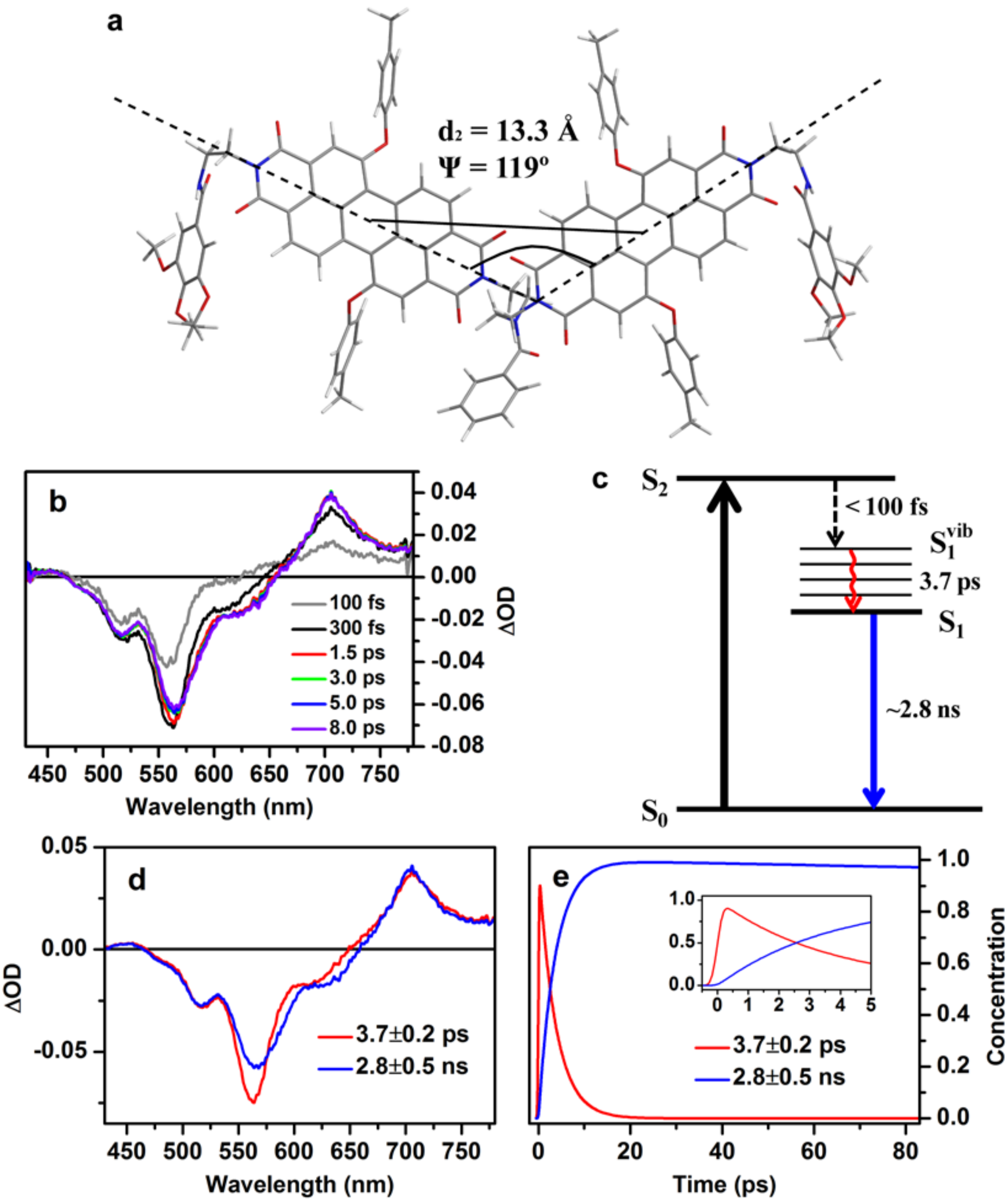

Figure S5. Energy-minimized structure of PDI-dimer (a). d_2 is the center-to-center distance between the two PDIs in one dimer; Ψ is the rotational displacement angle. Femtosecond transient absorption spectra for PDI-dimer in chloroform following excitation at 400 nm (b). Sequential reaction scheme for PDI-dimer (c), showing the relaxation pathways after excitation with 400 nm. EADS of PDI-dimer fitted with the corresponding sequential model (d). The associated population evolution curves of the EADS components for PDI-dimer (e). Inset shows the initial stages of evolutions of excited stated relaxation.

S5. The fitting parameters of PDI-monomer, -dimer and -hexamer from femtosecond transient absorption data

Table S2. Fitting parameters from global analysis of PDI-monomer, -dimer and -hexamer.

	τ_1	τ_2	τ_3
PDI-monomer	3.6±0.2 ps	2.5±0.5 ns	
PDI-dimer	3.7±0.2 ps	2.8±0.5 ns	
PDI-hexamer	1.2±0.1 ps	7.9±0.4 ps	20.0±1.0 ns

S6. Femtosecond transient absorption spectra at long delay times

Figure S6 shows femtosecond transient absorption spectra at long delay times. It is found that the spectra of both monomer and hexamer show no obvious changes at long delay times. Since in Figure 2 spectral evolution within first several picoseconds is shown, Figure S6 presents the complementary spectra for the transient absorption with long delay times for both monomer and hexamer.

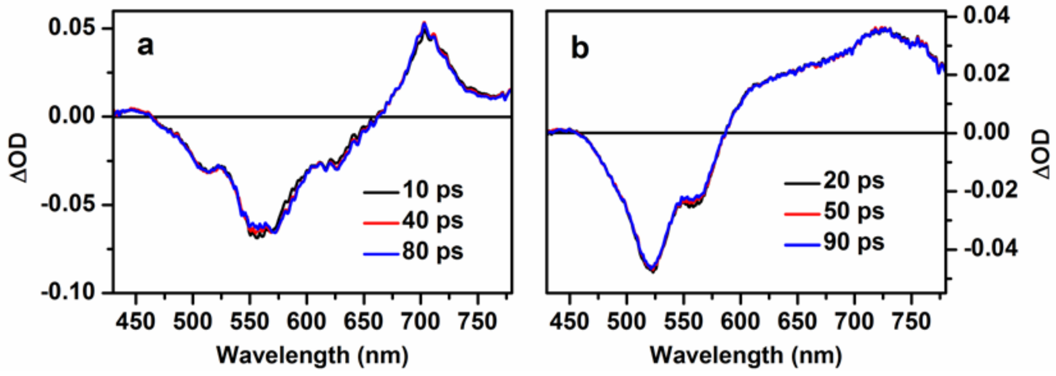

Figure S6. Femtosecond transient absorption spectra at long delay times for PDI-monomer (a) and PDI-hexamer (b) in chloroform following excitation at 400 nm.

S7. Kinetics at selected single wavelengths from femtosecond transient

absorption spectra for showing the quality of global fitting

In order to show the quality of global fitting, kinetics at selected single wavelengths are plotted together with a global fit of all the collected time traces in Figure S7, S8 and S9 for PDI-monomer, -dimer and -hexamer.

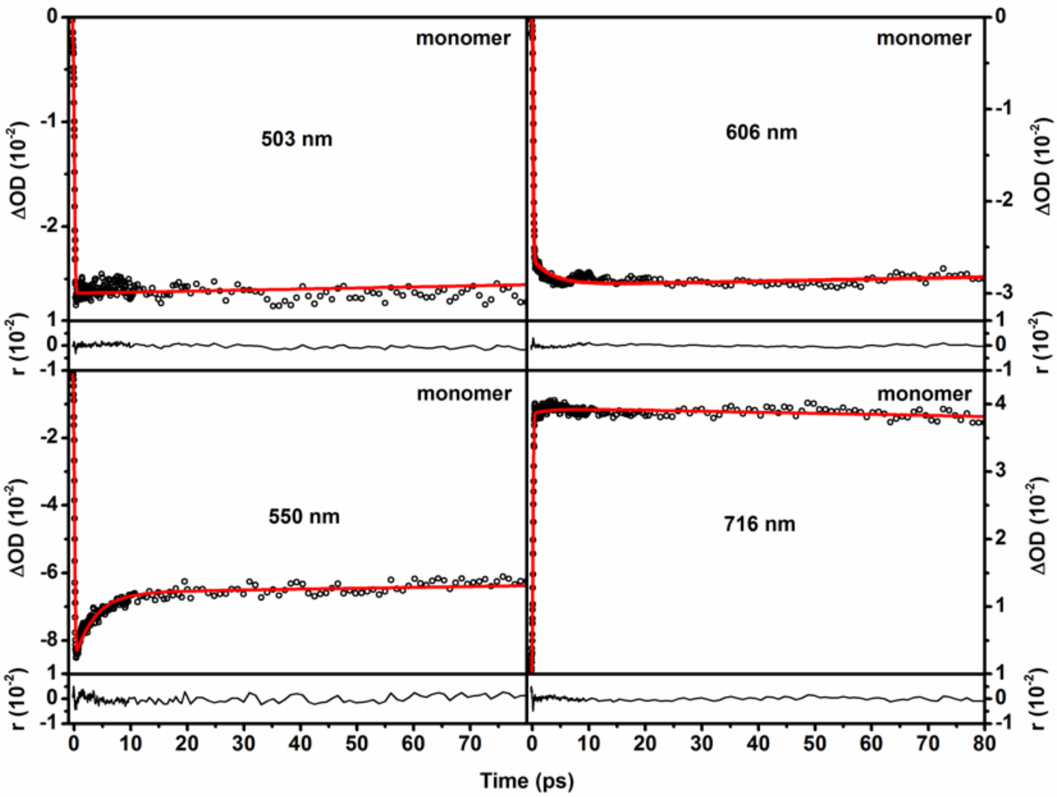

Figure S7. Kinetics at selected single wavelengths of PDI-monomer. Fitting curves and residuals of the fitting are also shown. The traces are fitted with the sequential model described in Figure 3a in the Text.

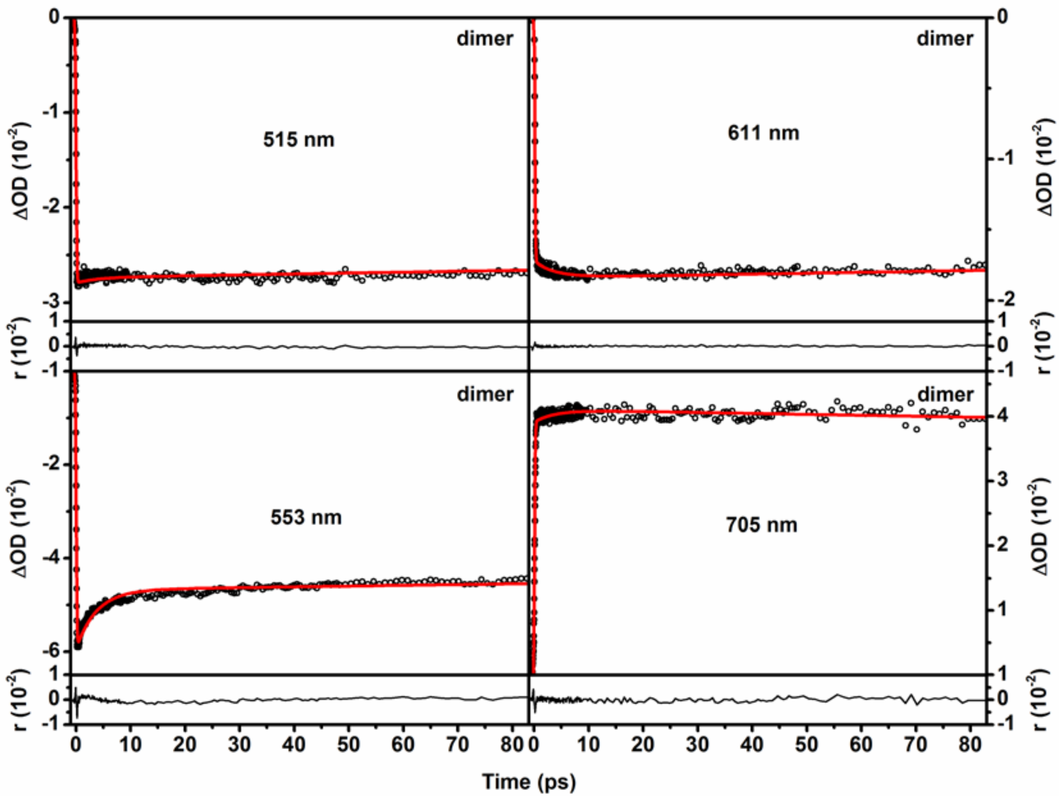

Figure S8. Kinetics at selected single wavelengths of PDI-dimer. Fitting curves and residuals of the fitting are also shown. The traces are fitted with the sequential model described in Figure S5c.

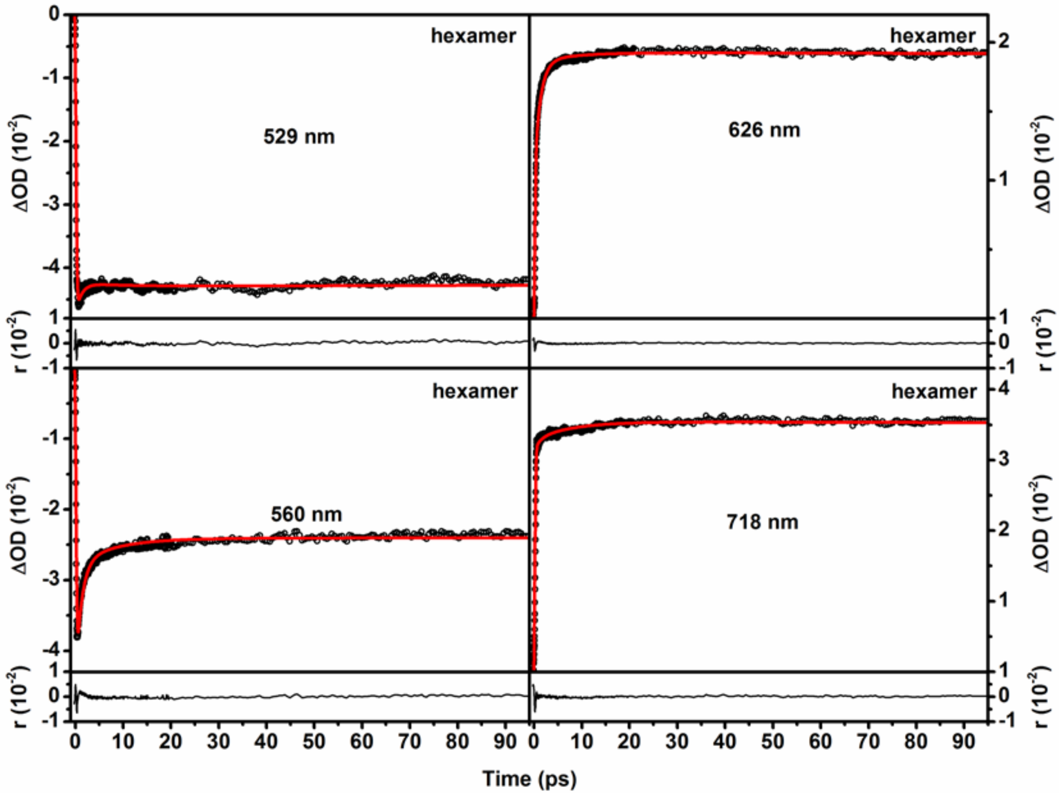

Figure S9. Kinetics at selected single wavelengths of PDI-hexamer. Fitting curves and residuals of the fitting are also shown. The traces are fitted with the sequential model described in Figure 3b in the Text.