Difference in the Photophysical Properties of a Perylenetetracarboxylic Diimide Dimer and a Hexamer Linked by the Same Hexaphenylbenzene Group

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Supporting Information
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1. Methods for the femtosecond transient absorption measurement
2. Absorption spectra of 6PDI at different temperatures and different concentrations
3. Transient absorption spectra of 2PDI, 6PDI and Monomer
1. **General methods for the femtosecond transient absorption experiments**

The transient absorption spectra were measured using homemade femtosecond broadband pump-probe setup. Briefly, a regeneratively amplified Ti:sapphire laser (Coherent Legend Elite) produces 40 fs, 1mJ pulses at a 500 Hz repetition rate with a spectrum centered at 800 nm and a bandwidth of 40 nm FWHM. The output from the amplifier is split by a 90/10 beam splitter into pump and probe beams. A portion of the 800-nm fundamental light was doubled in a 0.5 mm thick BBO (type I) crystal to provide the 400 nm pump pulse. About 100 nJ pulses at 400 nm was used for excitation. A synchronized optical chopper (New Focus Model 3501) with a frequency of 250 Hz is inserted into the pump beam path in order to record spectra that are classified as pumped and not-pumped spectra, thereby reducing background effects. Every spectrum is recorded 200 times and the average spectrum is used in further data processing. The probe beam at 800 nm is sent to a variable optical delay line, which comprises of a retro-reflector mirror on a computer controlled precision translation stage with a temporal resolution of 2 fs. The probe beam is then focused on either a 1mm sapphire plate or a 2-mm-thick water cell to generate a white light continuum (WLC). The WLC provides a usable probe source between 420 and 750 nm selected by a bandpass filter. The WLC was then split into two beams using a broadband 50/50 beam splitter for reference and signal beams. The signal is focused into a flow cell with 1mm path length and spatially and temporally overlapped with the pump beam at 400 nm in the liquid sample, while the reference beam is passed through the unexcited volume of the sample. Both reference and signal beams after the sample are focused into optical fibers of a dual-channel spectrometer (Avantes AvaSpec-2048-2-USB2) triggered from the same synchronized optical chopper driver at 500 Hz. In all measurements the mutual polarization of pump and probe beams was set to the magic angle.
Using the two-beam method, a few algorithms of data acquisition can be applied with the most common being a relative normalization of the spectral intensity of the signal to the spectral intensity of the reference. For each pump pulse, spectral intensities of the signal and the reference without any excitation in the sample, $I_{\text{off prob}}$ and $I_{\text{off ref}}$, respectively, and $I_{\text{on prob}}$ and $I_{\text{on ref}}$, in the presence of the pump, are measured. Then the $\Delta OD$ of the transient absorption (for a given time delay) can be calculated from the following formula:

$$
\Delta OD(t, \lambda) = \log\left( \frac{I_{\text{off prob}}(t, \lambda)}{I_{\text{on prob}}(t, \lambda)} \times \frac{I_{\text{on ref}}(t, \lambda)}{I_{\text{off ref}}(t, \lambda)} \right)
$$

(1)

The 0.1 mM solution of sample in spectral grade chloroform was prepared under dim light and circulated in a flow cell with a path length of 1 mm to ensure that a fresh sample volume was exposed to each pump pulse. A wavelength-dependent time-zero correction was performed to account for the group velocity dispersion of the probe beam.

The time-resolved anisotropic decay $r(t)$ was calculated from the decay curves under the parallel polarizations $I_{\|}(t)$ and perpendicular polarizations $I_{\perp}(t)$ of probe beam relative to the polarization of pump beam according to equation 2:[1,2]

$$
r(t) = \frac{I_{\perp}(t) - G \cdot I_{\|}(t)}{I_{\perp}(t) + 2G \cdot I_{\|}(t)}
$$

(2)

where $I_{\perp}$ and $I_{\|}$ represent signals with the polarizations of the pump and probe being mutually parallel and perpendicular, respectively. $G = I_{\perp}(t)/I_{\|}(t)$, when the excitation is vertically polarized.

Figure S1. The absorption spectra of 6PDI in toluene at different concentrations.

Figure S2. The absorption spectra of 6PDI in toluene at different temperature (°C)
Figure S3. Transient absorption spectra of monomer in dichloromethane at different time delay.

Figure S4. Transient absorption spectra of 2PDI in dichloromethane at different time delay.
Figure S5. Transient absorption spectra of 6PDI in dichloromethane at different time delay.