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Electronic Supplementary Information

Electron-Transporting Foldable Alternating Copolymers of Perylenediimide and Flexible Macromolecular Chains

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1. Absorption Spectroscopy

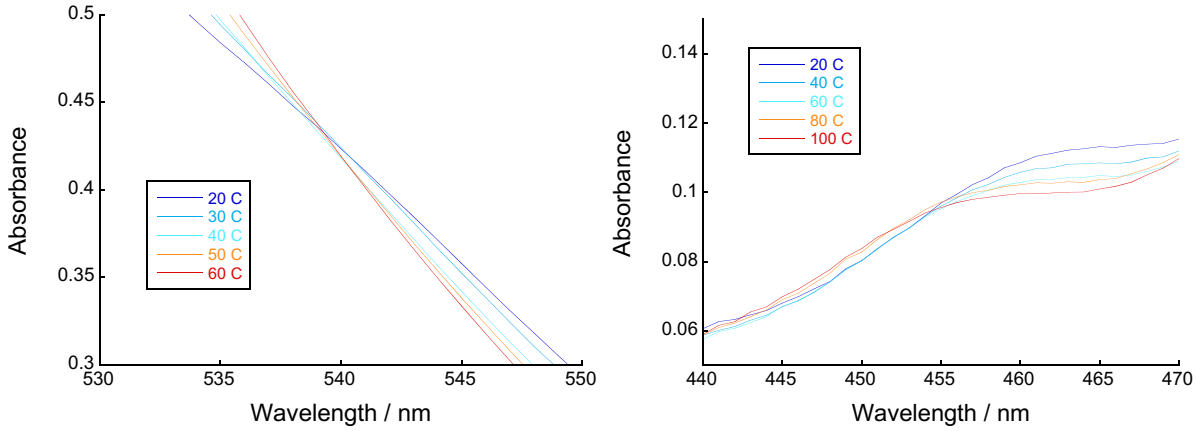

Figure S1. Enlarged spectra of **(PDI-PDMS$_{5000}$)$_n$** in THF (left) and toluene (right) at the temperature of 20–60 ºC (left) and 20–100 ºC (right).

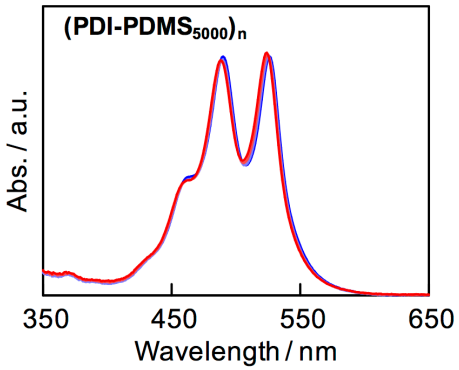

Figure S2. Variable-temperature absorption spectra of **(PDI-PDMS$_{5000}$)$_n$** in $CHCl_3$ at 10^{-5} M from 20 °C (blue) to 60 °C (red) at every 10 °C.

Discussion on Possibility of Concentration Changes upon Elevating Temperature

Thermal expansion of solvents was the term of consideration in elevating temperature under constant pressure. The volume expansion coefficient α for typical organic ethers:

$$\alpha = \frac{1}{V_m}\frac{\mathrm{d}V_m}{\mathrm{d}T},$$

ranges in α = 0.9–1.2 × 10^{-3} K^{-1}. Simultaneously, the optical path length of the quartz cuvette is increased upon heating. However, the value of $\alpha_{SiO2} \sim 5 \times 10^{-7}$ K^{-1} is small enough to be negligible for the absorbance changes. Assuming the case of these expansion coefficients, the temperature elevation from 20 to 60 °C may cause approx. 4 % volume expansion at maximum, which may cause a little reduction of concentration of the compound in the solvent. The coefficient for toluene is $\alpha = 1.05 \times 10^{-3}$ K^{-1}, suggesting almost identical change of concentration.

Quantitative estimates for the effects of thermal volume expansion are also examined by the precise trace of an isosbestic points under elevating temperature. **Figure S1** shows the enlarged view of absorption spectra observed for **(PDI-PDMS$_{5000}$)$_n$** in THF and toluene, respectively. The former shows an isosbestic point at 455 nm, the latter at 539 nm. The variation of the absorbance at these points are Abs = 0.097 ± 0.0015 (in THF) and 0.436 ± 0.003 (in toluene), suggesting the deviation less than 2 % in both solvents. The solutions are enclosed into a screw-cap cuvette for the spectroscopic meausrements, where liquid-vapor phases were in equilibrium at every temperature. The volume change was relaxed in the cuvette, and subsequent cuvette expansion led the smaller effects of volume expansion on the observed absorbance in the present case. Moreover, an example of VT absorption spectra of **(PDI-PDMS$_{5000}$)$_n$** in $CHCl_3$ was recorded, where the value of $\alpha = 1.21 \times 10^{-3}$ K^{-1} is almost identical to the case of THF and no distinct temperature-dependent change was observed. Overall, the observed temperature-dependent band-specific absorption changes are significant, indicating the contrastingly association/dissociation of contrastingly PDI chromophores.

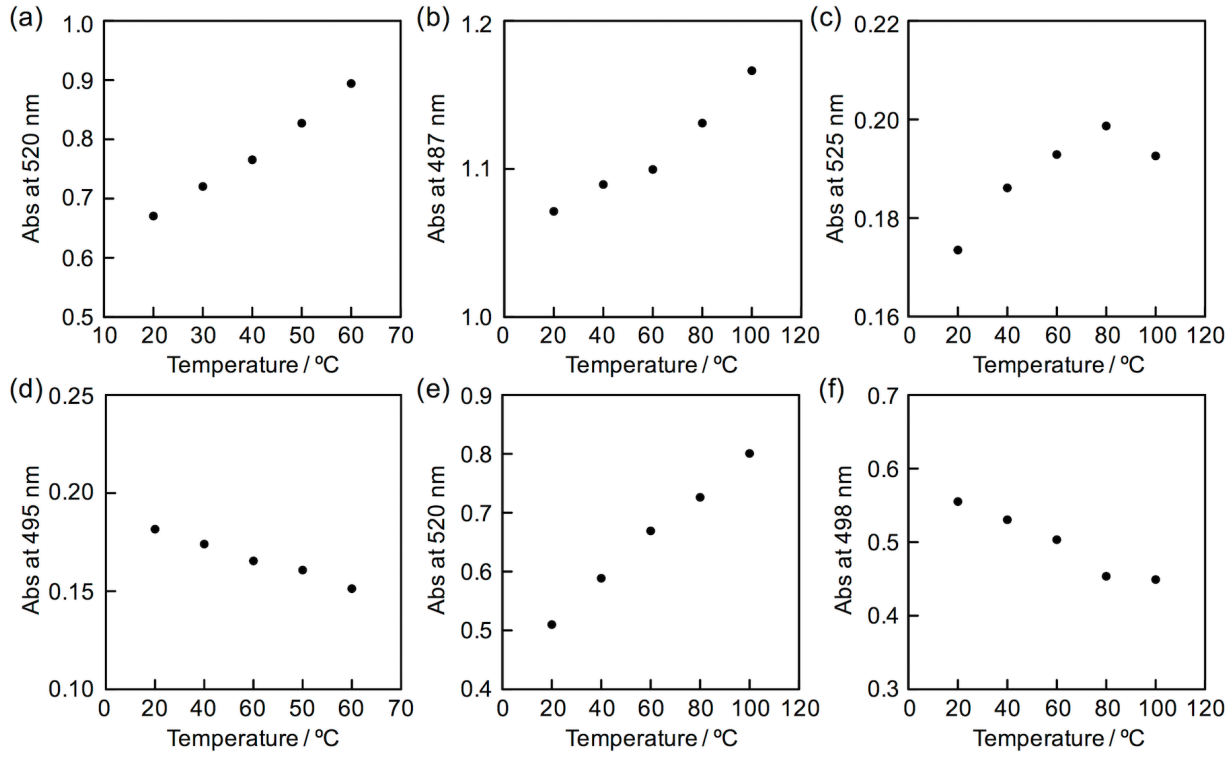

Figure S3. Intensity plots in variable-temperature absorption spectra for **(PDI-PDMS$_{5000}$)$_n$** in THF at (a) 520 nm and (b) 487 nm, **(PDI-PDMS$_{5000}$)$_n$** in toluene at (c) 525 nm and (d) 495 nm, and **(PDI-PEG$_{2000}$)$_n$** in toluene at (e) 525 nm and (f) 498 nm.

2. Dynamic Light Scattering

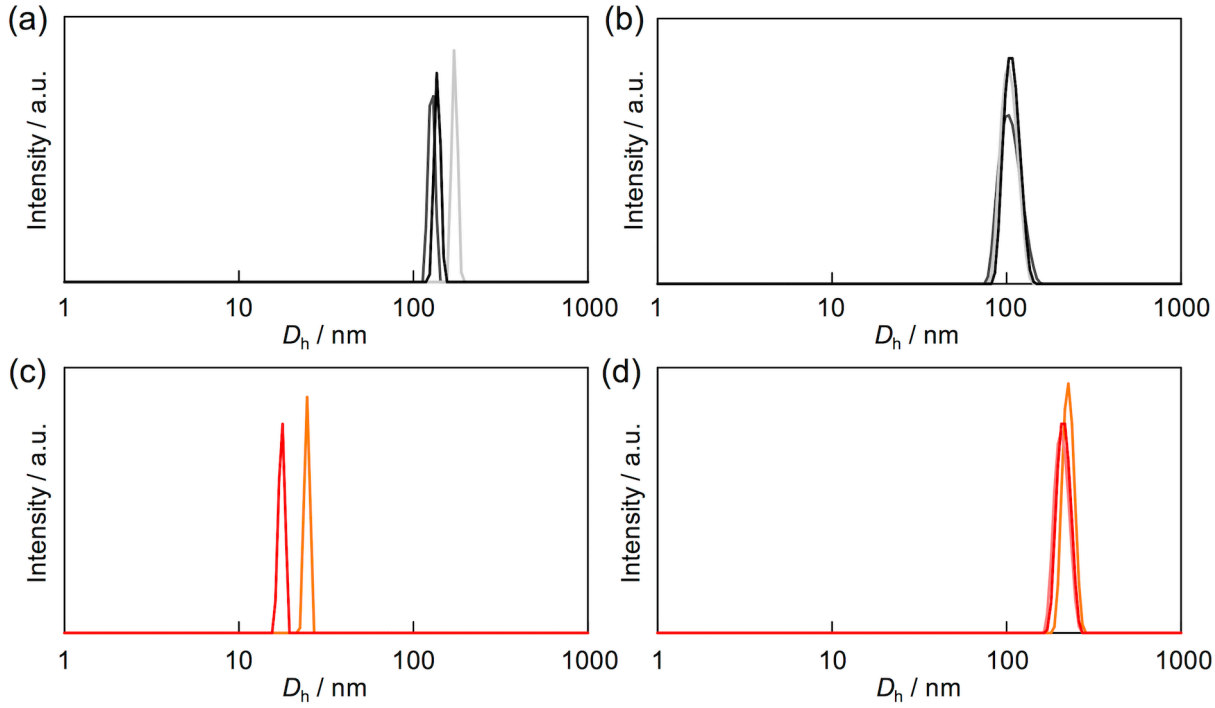

Figure S4. Hydrodynamic diameters of **(PDI-PDMS$_{5000}$)$_n$** typically observed in (a) $CHCl_3$ and (c) THF analyzed by dynamic light scattering. Hydrodynamic diameters of **(PDI-PPG$_{4000}$)$_n$** typically observed in (b) $CHCl_3$ and (d) THF. The size distribution of **(PDI-PDMS$_{5000}$)$_n$** in THF is smaller than that in $CHCl_3$, which may reflect the folding conformation in THF.

3. Differential Scanning Calorimetry

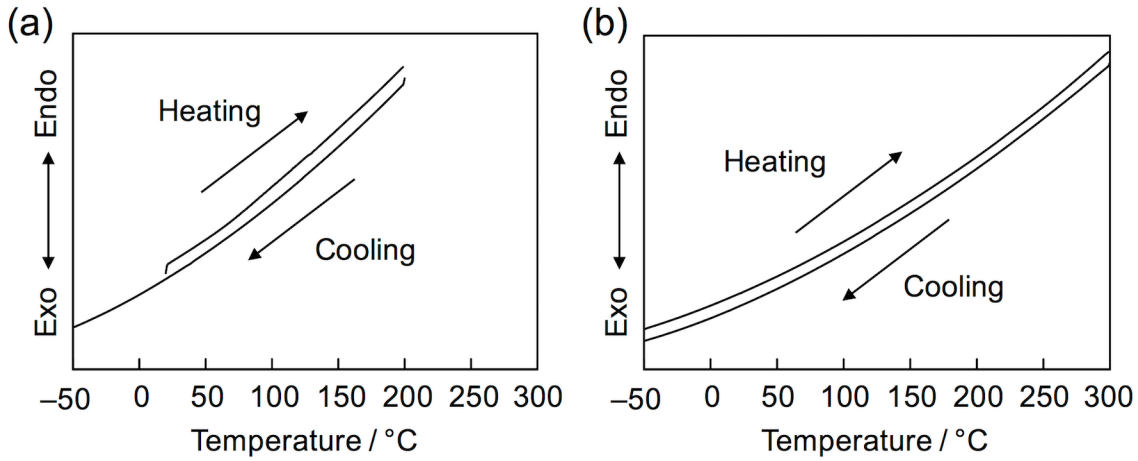

Figure S5. DSC traces of **(PDI-PDMS$_{5000}$)$_n$** at (a) 1st and (b) 2nd heating–cooling cycles. No obvious melting point and glass transition temperature was observed.