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

Supporting Information for:

Cooperative Supramolecular Polymerization of a Perylene Diimide Derivative and its Impact on Electron-transporting Property

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Temperature dependent study and analysis: Solution of **PDI-1** in decalin (1.25 x 10^{-5} M) was prepared following the above mentioned protocol and transferred to a quartz cuvette and heated by a peltier device at 358K for 15 minutes prior to the experiment. The solution was subjected to a cooling heating cycle and absorption at a single wavelength (482 nm) was monitored as function of temperature (358 K to 298 K at 1 K/min) by Perkin-Templab software connected to the UV/Vis machine. Mole fraction of aggregates (α_{agg}) at different time of photo-irradiation was estimated using the following.

$$\alpha_{(agg)} = \frac{A(T) - A(\min)}{A(\max) - \mathrm{A}(\min)} ------------(1)$$

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Where *A* (max), *A* (min) and *A* (*T*) stand for band (482 nm) intensity maximum, minimum and recording temperature.

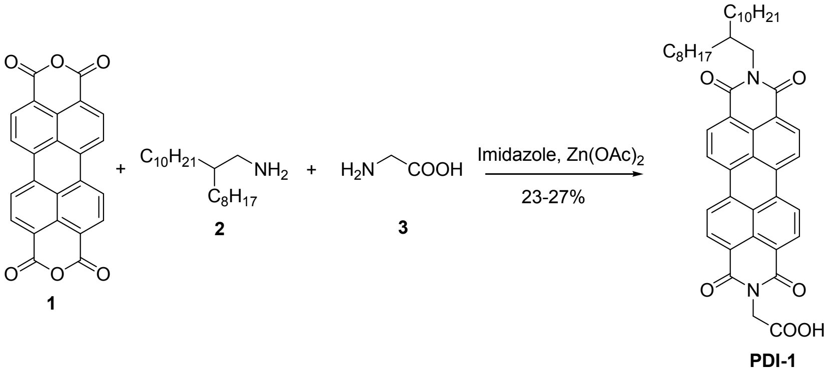
The cooling curves were attempted to fit either in the isodesmic or cooperative model.[1] In the isodesmic model, Boltzmann function was used and the growth sigmoidal was attempted to fit using Origin 8.0 software. However, the data failed to fit in isodesmic model. Thus fitting of the data was attempted in cooperative model using MATLAB. First elongation and nucleation regime were separated and data was fitted by using two known equations as per prior reports.[2-3] Next, we have attempted to fit non-sigmoidal cooling curve of **PDI-1** in decalin using variable size nucleation-elongation model. The nucleation and elongation regime are separated by elongation temperature (T_e). This model depicts the supramolecular polymerization is initiated by thermally activated (where $T > T_e$) nucleation step (expressed with dimensionless equilibrium constant K_a, equation 3) i.e., linear oligomerization of monomers which indeed an unfavorable step. Subsequently, the activated oligomers (where $T < T_e$) undergo supramolecular polymerization i.e., elongation (expressed with dimensionless equilibrium constant K_e, equation 2) and a highly favorable step.

$$\alpha_{agg} = \alpha_{const}\left[1-\exp(\frac{-h_e}{RT_e^2}(T-T_e)\right]----------------(2)$$

$$\alpha_{agg} = \alpha_{const}\left[\sqrt[3]{K_a}\exp[(\frac{2}{3.\sqrt[3]{K_a}}-1)\frac{-h_e}{RT_e^2}(T-T_e)]\right]-------(3)$$

where h_e represents released enthalpy due to non-covalent interaction, α_{const} is a constant which ensures $\alpha_{agg}/\alpha_{const}$ does not exceed unity and R is universal gas constant. K_a is a dimensionless equilibrium constant which measures extent of cooperativity. T_e and T are the elongation and absolute temperature respectively. The cooling curve of **PDI-1** was independently fitted with equation 2, 3 for elongation and nucleation regime, respectively. Indeed all data accurately fitted over the entire temperature range and thermodynamic parameters on self-assembly.

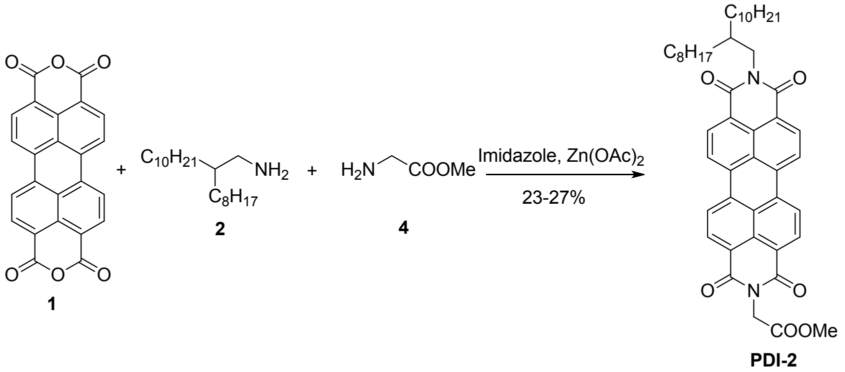
Synthesis of **PDI-1:**



Scheme S1. Synthesis of **PDI-1**

A mixture of perylene dianhydride **1** (0.5 g, 1.27 mmol), glycine **3** (0.095 g, 1.27 mol), branched amine **2** (0.38 g, 1.27 mmol), zinc acetate (0.5 g, 2.2 mmol), and imidazole (5.0 g) was stirred under argon at 140 °C for 18 h. After being cooled to room temperature, the reaction mixture was poured into 50 mL of methanol. The precipitate was collected through filtration, washed with methanol and the crude product was purified by silica gel column chromatography using $CHCl_3$/acetic acid (0.5%) as eluents to produce 0.25 g (27% yield) of **PDI-1** as red solid. ^1H NMR ($CDCl_3$ and 10% TFA, 500 MHz) δ: 8.83-8.78 (m, 8H); 5.17 (s, 2H); 4.21 (d, *J* = 7.5 Hz, 2H); 2.03-2.01 (m, 2H); 1.39-1.22 (m, $\underline{CH_2}$, 32H), 0.85-0.82 (m, $\underline{CH_3}$, 6H); ^{13}C NMR ($CDCl_3$ and 10% TFA, 400 MHz) δ: 163.76, 160.1, 159.76, 159.42, 159.08, 134.97, 132.64, 132.39, 125.02, 124.05, 123.71, 123.31, 122.37, 119.00, 115.81, 118.07, 113.64, 111.27, 36.82, 34.74, 32.08, 32.02, 31.88, 31.50, 30.34, 30.14, 29.85, 29.81, 29.78, 29.51, 26.63, 22.84, 20.74, 14.23, 14.20.

Synthesis of **PDI-2:**



Scheme S2. Synthesis of **PDI-2**

A mixture of perylene dianhydride **1** (0.5 g, 1.27 mmol), glycine methyl ester **4** (0.095 g, 1.27 mol), branched amine **2** (0.38 g, 1.27 mmol), zinc acetate (0.5 g, 2.2 mmol), and imidazole (5.0 g) was stirred under argon at 140 °C for 18 h. After being cooled to room temperature, the reaction mixture was poured into 50 mL of methanol. The precipitate was collected through filtration, washed with methanol and the crude product was purified by silica gel column chromatography using $CHCl_3$/methanol(4%) as eluents to produce 0.35 g (27% yield) of **PDI-2** as red solid. ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.60-8.51 (m, *a*, 8H); 5.07 (s, 2H); 4.38 (d, *J* = 7.5 Hz, 2H); 3.828 (s, 3H), 2.00 (b, *2H*); 1.39-

1.22 (m, $\underline{CH_2}$, 32H), 0.85-0.82 (m, $\underline{CH_3}$, 6H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 163.75, 163.09, 135.11, 134.33, 131.81, 131.51, 123.65, 123.39, 123.05, 53.54, 36.82, 32.06, 31.96, 30.20, 29.79, 29.48, 26.69, 22.81, 14.23.

Additional Figures:

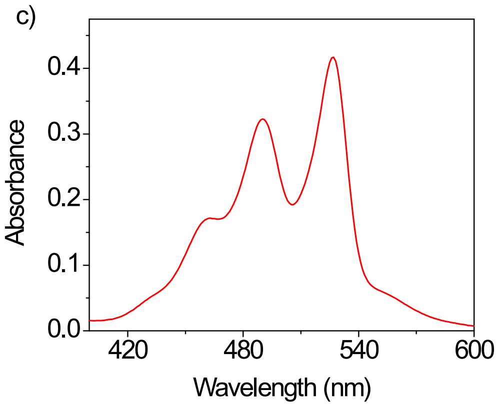


Fig. S1 Absorption spectra of **PDI-1** in $CHCl_3$, $c = 1.0 \times 10^{-5}$ M, $l = 1.0$ cm, $T = 25$ °C. Spectroscopic grade solvent was used which is devoid of any ethanol as the stabilizer.

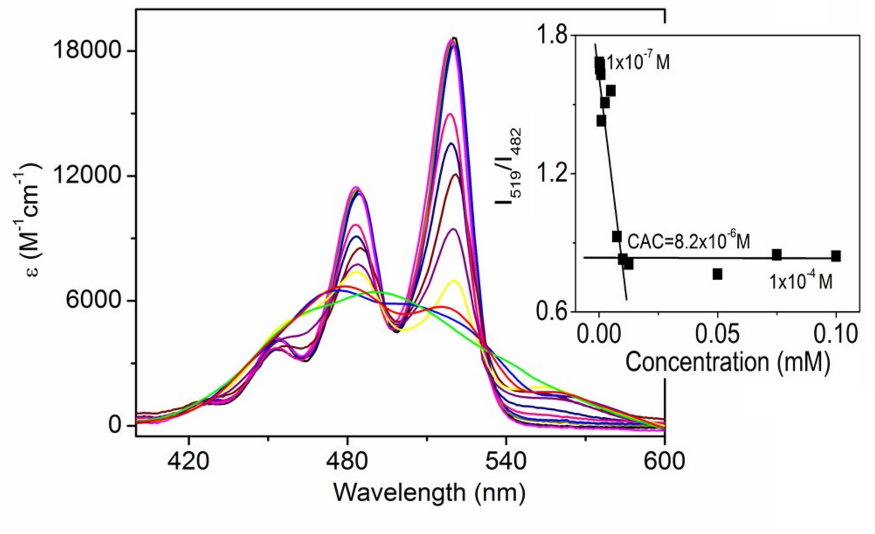


Fig. S2 Concentration dependent absorption spectra of **PDI-1** in decalin (l= 1 cm), (inset) -Plot of ε vs concentration

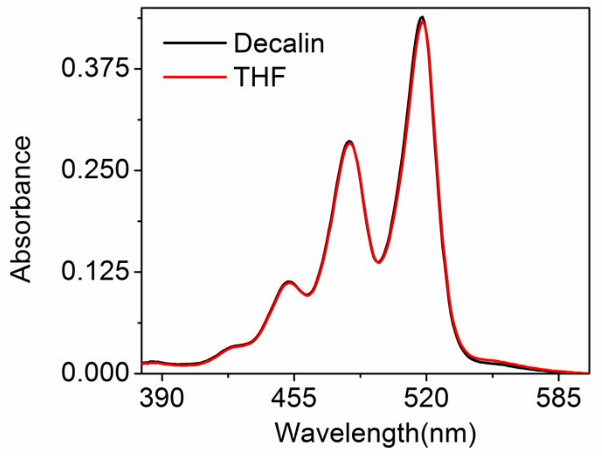


Fig. S3. Solvent-dependent UV-vis absorption spectra of **PDI-2** in THF (red) and decalin (black), $c = 1 \times 10^{-5}$ M, path length 1 cm.

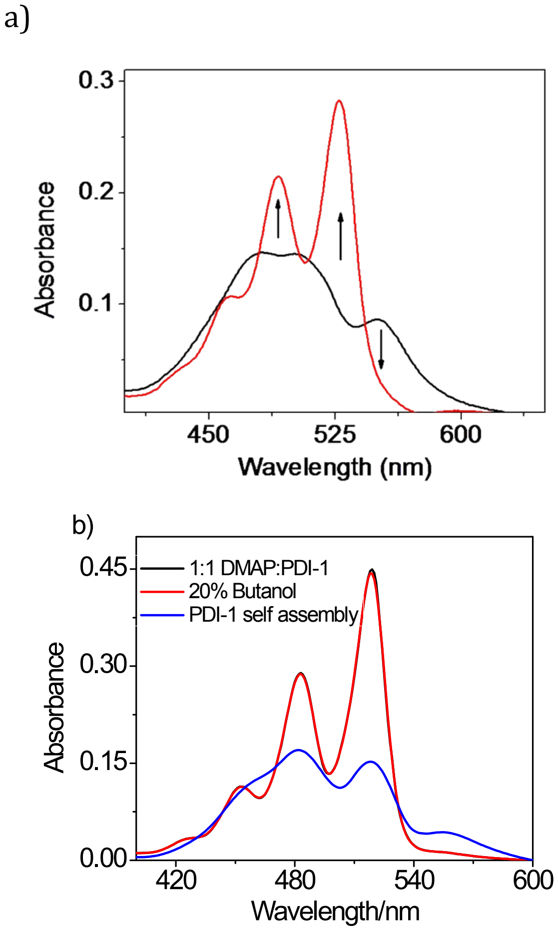


Fig. S4. a) Absorption spectra of **PDI-1** in decalin (black) and after 1% (v/v) TFA addition (red), $c = 1 \times 10^{-5}$ M; b) Absorption spectra of **PDI-1** in decalin (blue) and in presence of DMAP and butanol, $c = 1.25 \times 10^{-5}$ M; In all measurements $l = 1.0$ cm, $T = 25$ °C.

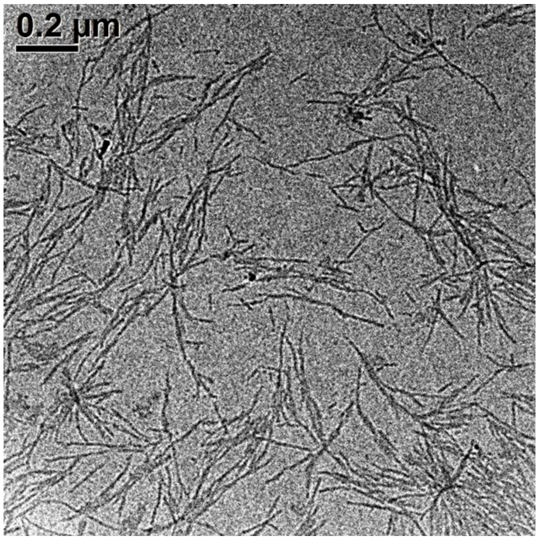


Fig. S5. Additional HRTEM data of PDI-1 in decalin

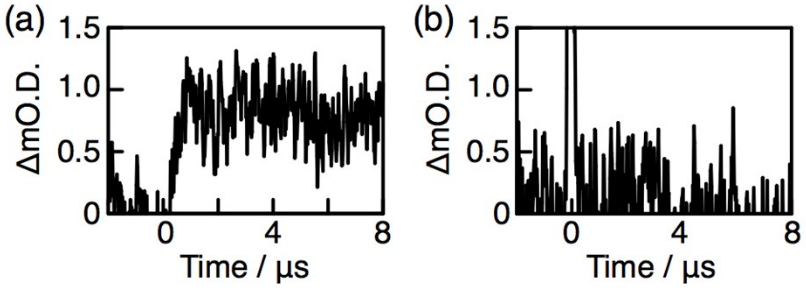


Fig. S6. Kinetic traces of transient absorption observed at (a) 710 nm and (b) 590 nm (right) in a dropcast film of **PDI-1** under an excitation at 355 nm. The spike peak at 0 µs in (b) represents an artifact originating from the strong emission.

References:

1. H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme, J. D. Williams, *J. Chem. Soc. Perkin Trans*., 1985, **2**, 607.
2. M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F.A. de Greef, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Chem. Eur. J.,* 2010, **16**, 362.
3. P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Science,* 2006, **313**, 80.