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Supporting Information

Control of H- and J-Type π-Stacking by Peripheral Alkyl Chains and Self-Sorting Phenomena in Perylene Bisimide Homo- and Heteroaggregates

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UV/Vis Spectra:

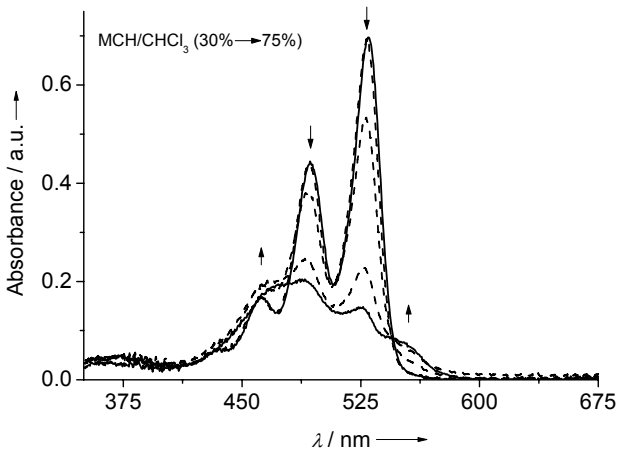

Figure S1. Solvent-dependent UV/Vis absorption spectra of **PBI-2** in MCH/$CHCl_3$ mixtures from 30:70 to 75:25 at a concentration of 1 x 10^{-5} M at 25 °C. Arrows indicate the spectral changes with increasing amount of methylcyclohexane (MCH) in solution.

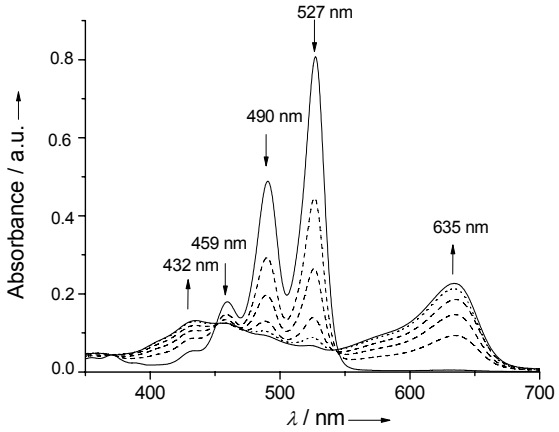

Figure S2. Solvent-dependent UV/Vis absorption spectra of **PBI-3** in MCH/$CHCl_3$ mixtures from 50:50 to 90:10 at a concentration of 1 x 10^{-5} M at 25 °C. Arrows indicate the spectral changes with increasing amount of MCH in solution.

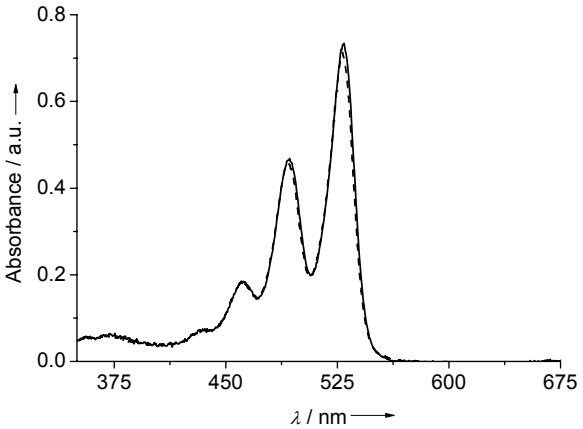

Figure S3. Solvent-dependent UV/Vis absorption spectra of **PBI-5** at a concentration of 1 x 10^{-5} M and temperature at 25 °C (solid line: chloroform, dashed line: MCH).

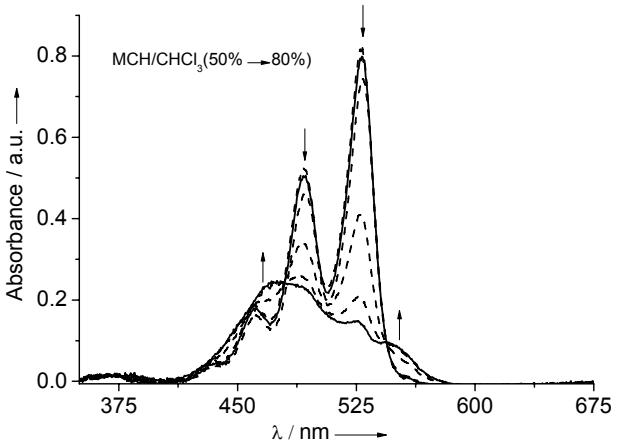

Figure S4. Solvent-dependent UV/Vis absorption spectra of **PBI-6** in MCH/$CHCl_3$ mixtures from 50:50 to 80:20 at a concentration of 1 x 10^{-5} M at 25 °C. Arrows indicate the spectral changes with increasing amount of MCH in solution.

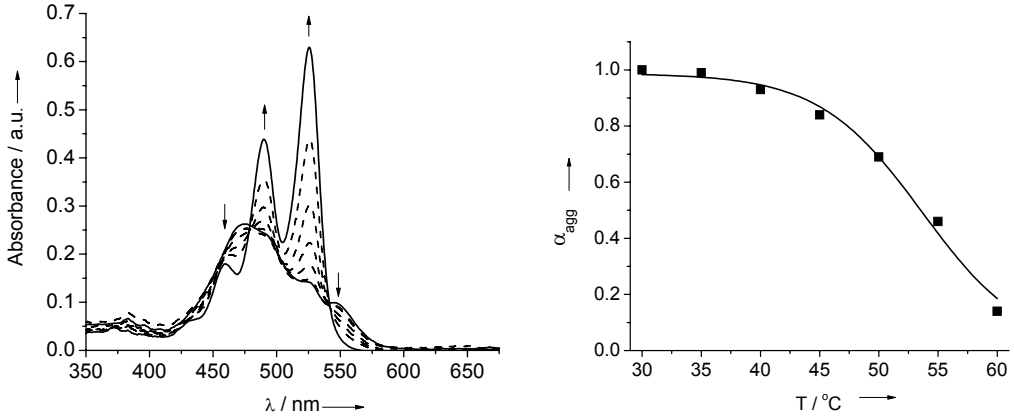

Figure S5. Variable-temperature UV/Vis studies for **PBI-1** in 80:20 MCH/$CHCl_3$ at a concentration of 1 x10^{-5} M. Left: Original spectral variations, arrows indicate spectral changes with increasing temperature. Right: Plot of mole fraction of aggregate as a function of temperature (Sigmoidal fit of the data points was achieved using Boltzmann function).

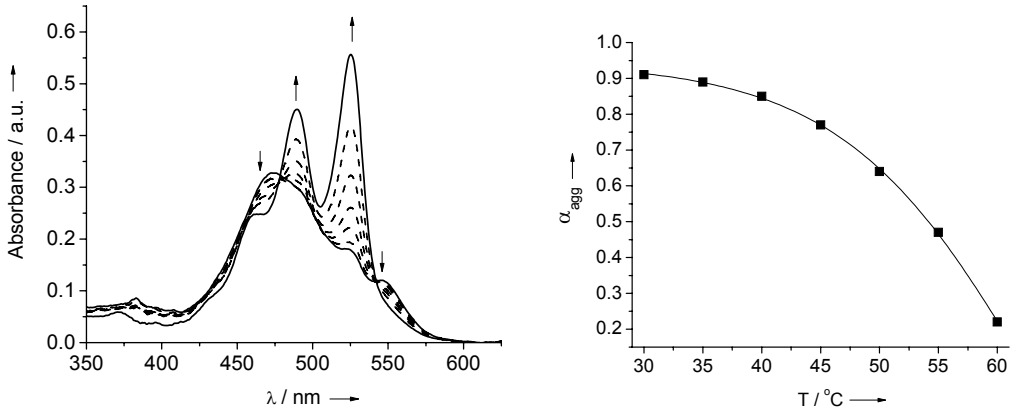

Figure S6. Variable-temperature UV/Vis studies for **PBI-2** in 80:20 MCH/$CHCl_3$ at a concentration of 1 x 10^{-5} M. Left: Original spectral variations, arrows indicate spectral changes with increasing temperature. Right: Plot of mole fraction of aggregate as a function of temperature (Sigmoidal fit of the data points was achieved using Boltzmann function).

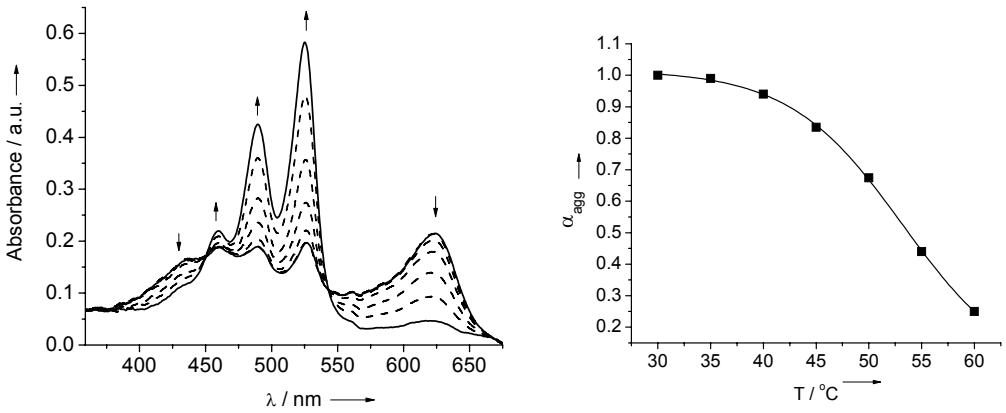

Figure S7. Variable-temperature UV/Vis studies for **PBI-3** in 80:20 MCH/$CHCl_3$ at a concentration of 1 x 10^{-5} M. Left: Original spectral variations, arrows indicate spectral changes with increasing temperature. Right: Plot of mole fraction of aggregate as a function of temperature (Sigmoidal fit of the data points was achieved using Boltzmann function).

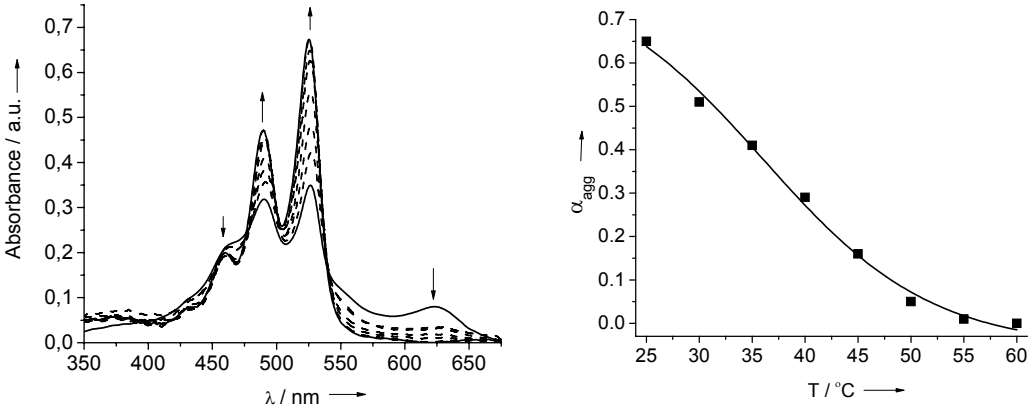

Figure S8. Variable-temperature UV/Vis studies for **PBI-7** in 80:20 MCH/$CHCl_3$ at a concentration of 1 x10^{-5} M. Left: Original spectral variations, arrows indicate spectral changes with increasing temperature. Right: Plot of mole fraction of aggregate as a function of temperature (Sigmoidal fit of the data points was achieved using Boltzmann function).

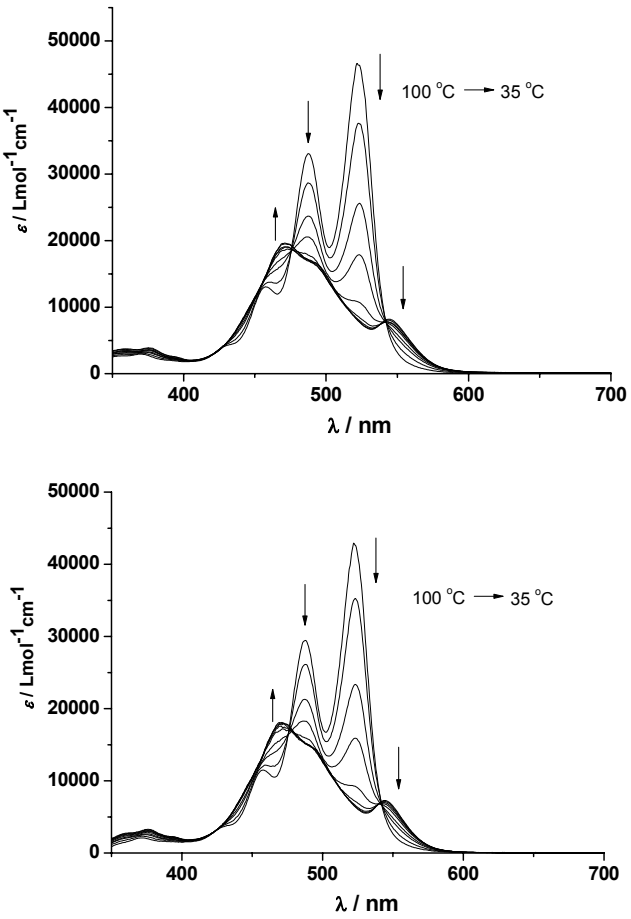

Figure S9. Variable-temperature UV/Vis studies for **PBI-1** in (*R*)-limonene (top) and (*S*)-limonene (bottom) at a concentration of 5 x 10^{-5} M. Arrows indicate spectral changes upon changing the temperature from 100 °C to 35 °C.

CD Spectra:

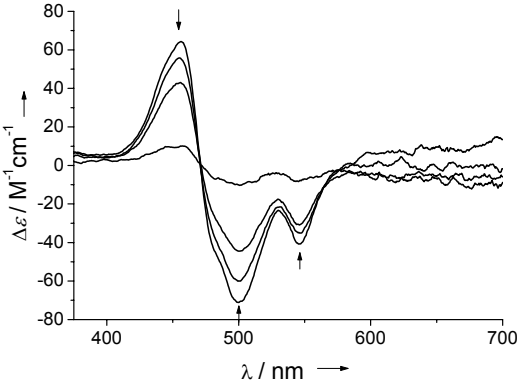

Figure S10. Temperature-dependent CD spectra of PBI-6 in MCH/CHCl3 mixture (80:20) at a concentration of 1 x 10-5 M. Arrows indicate the spectral changes with increasing temperature (30 °C to 60 °C).

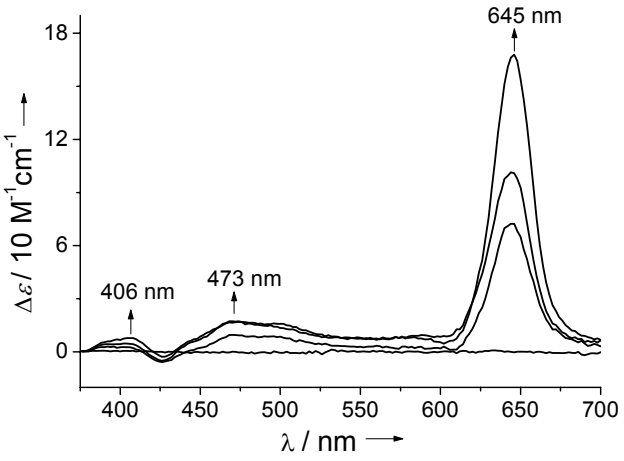

Figure S11. Solvent-dependent CD spectra of **PBI-3** in MCH/$CHCl_3$ mixtures from 55:45 to 80:20 at a concentration of 1 x 10^{-5} M at 25 °C. Arrows indicate the spectral changes with increasing amount of MCH.

LD spectra:

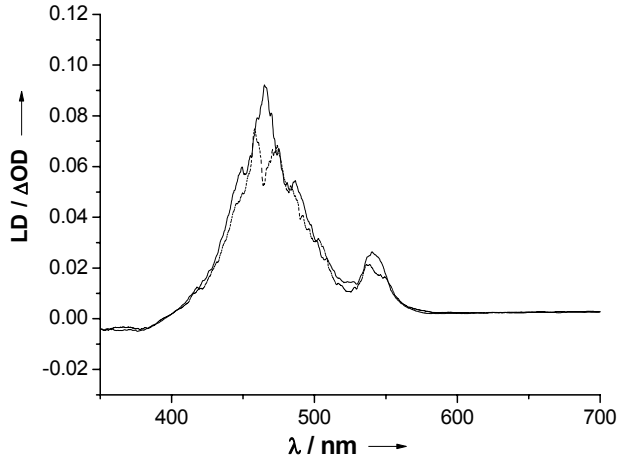

Figure S12. LD spectra of **PBI-1** (5×10^{-5} M, in toluene) obtained under stirring at 1300 rpm; solid and dash lines indicate the spectra for the clockwise and anticlockwise stirring direction, respectively.

AFM Images:

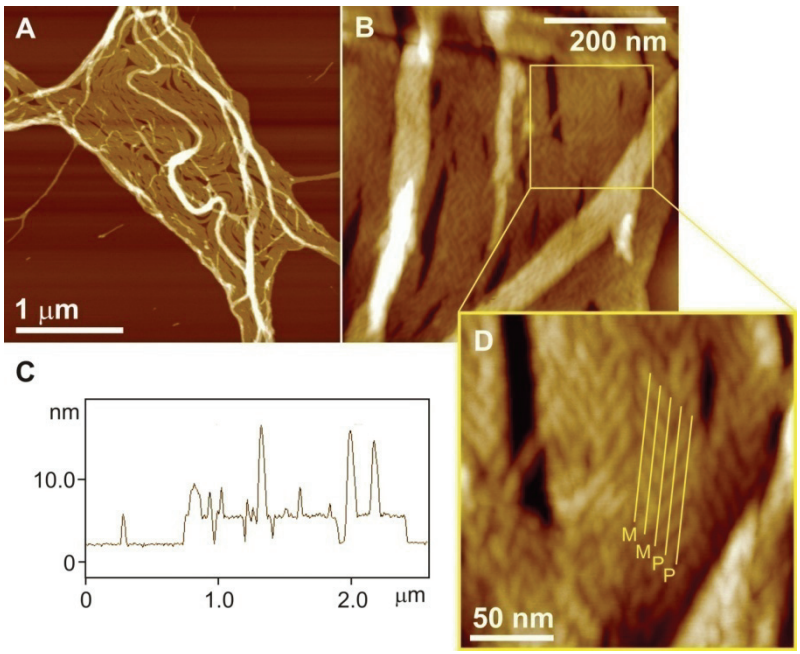

Figure S13. AFM images (A, B, D: height image, C: cross sectional analysis) of **PBI-6**. Diluted gel (0.3 mM) in toluene was spin-casted on mica before taking AFM images.

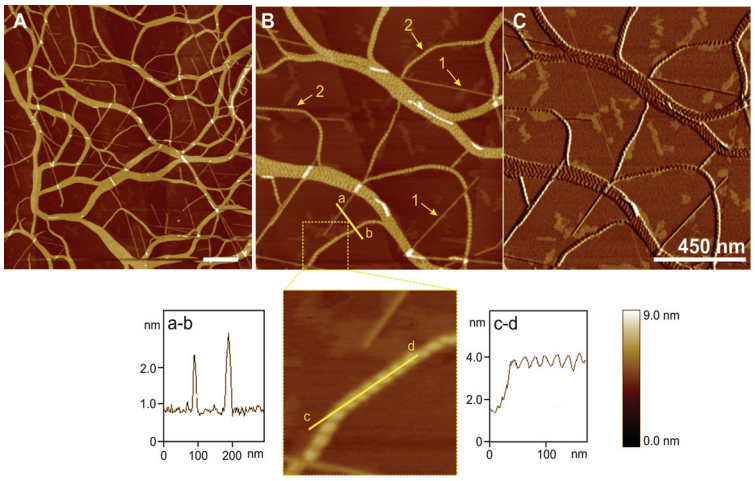

Figure S14. AFM images of a film spin-coated from cold (room temperature) solution of **PBI-1** in (*S*)-limonene (1×10^{-4} M) onto HOPG. A, B: height images, C: phase image. In images A, B, and C the scale bar corresponds to 450 nm and the z scale in A and B is 9 nm. Arrows 1 point at non-helical structures. Arrows 2 point at helical fibers.