

Supporting information

Transformation from Helical to Layered Supramolecular Organization of Asymmetric Perylene Diimides via Multiple Intermolecular Hydrogen Bonding

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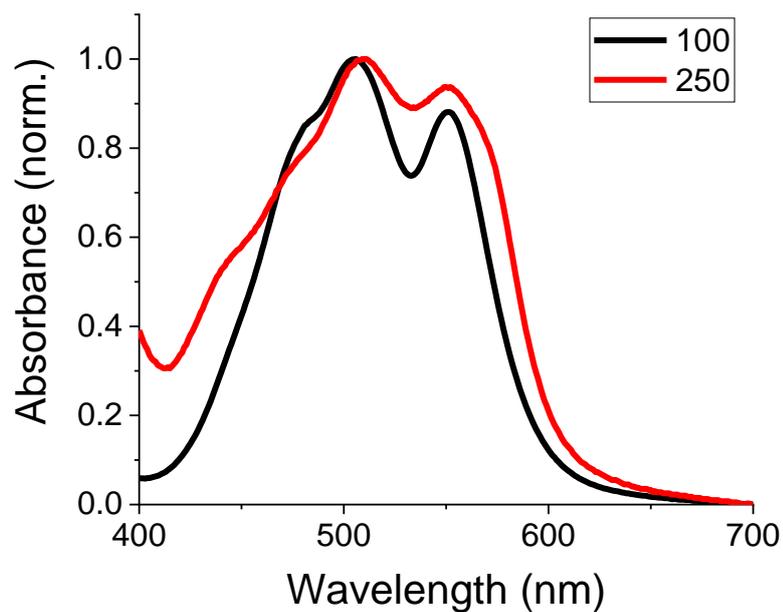


Figure S1. UV-vis absorption spectra of PDI **9** thin films after annealing at 100 °C and 250 °C. All films were spin-coated from 3 mg mL⁻¹ chloroform solutions.

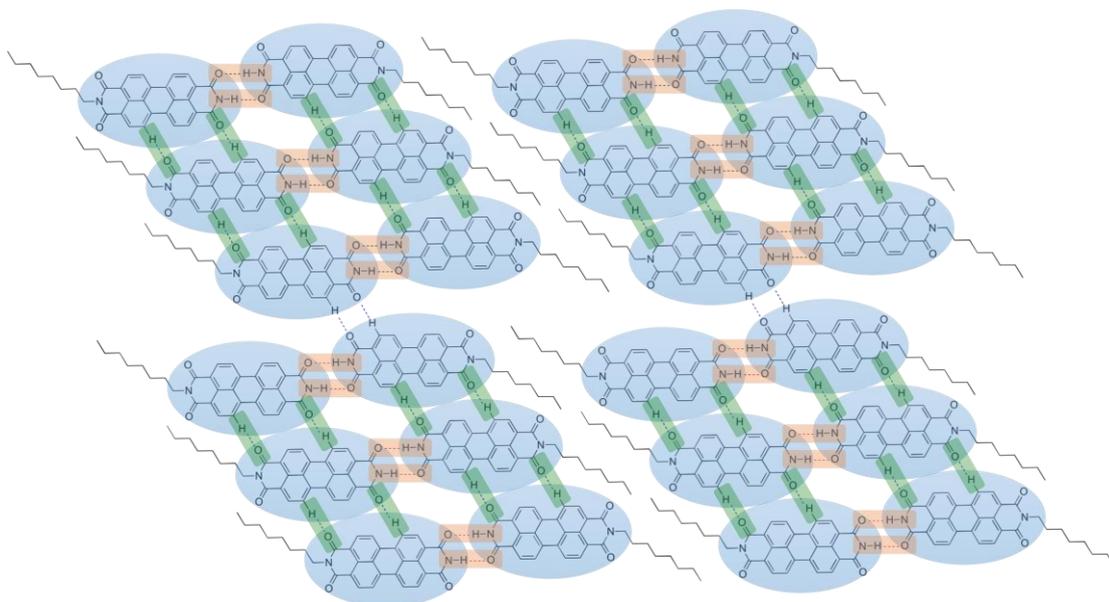


Figure S2. A simple schematic model for different types of supramolecular interactions involved in the self-assembled monolayer of **1** according to the STM results.

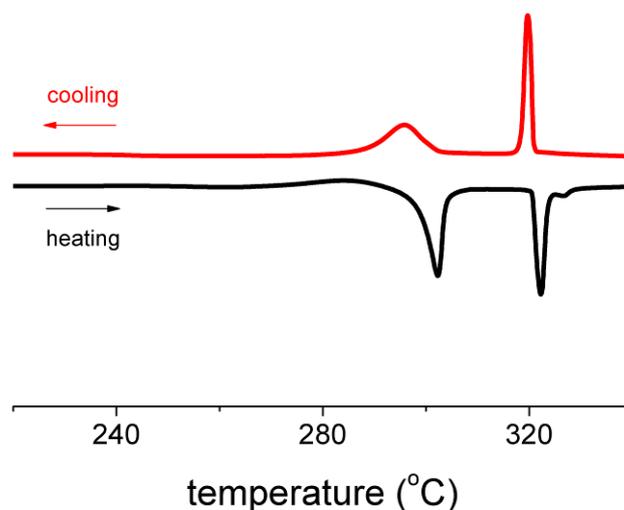


Figure S3. DSC plot of PDI **9** at a scan rate of 5 °C/min.

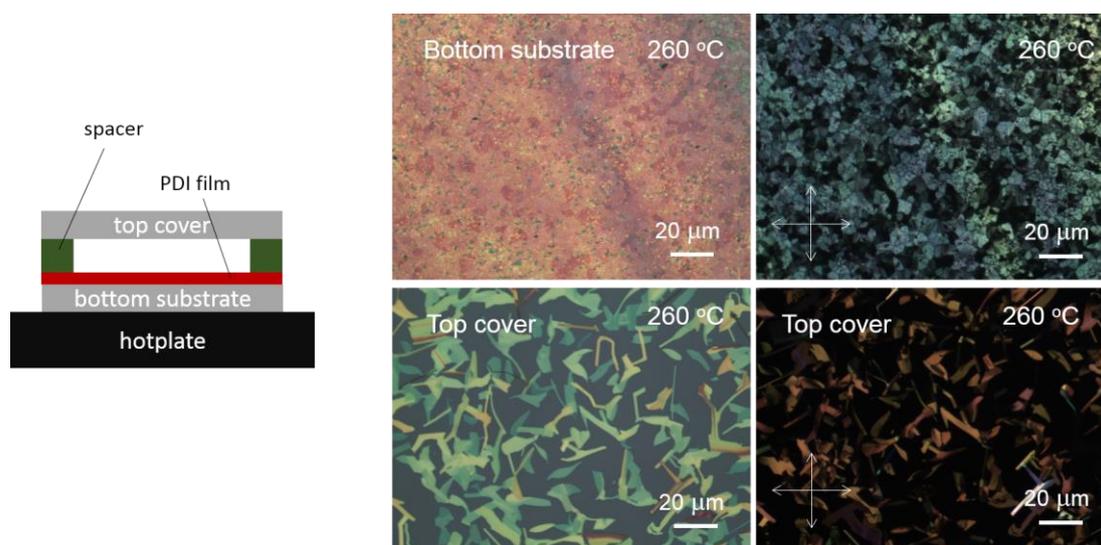


Figure S4. Slow sublimation of PDI **9** at 260 °C. Left: PDI film was drop-cast onto the top surface of bottom substrate, while there is no material on the bottom surface of the top cover. The spacer is around 3 mm in height. Both top cover and bottom substrate are SiO₂ wafers. Upon annealing at 260 °C, molecules are slowly sublimated onto the bottom surface of top cover as evident from the optical microscopy images.

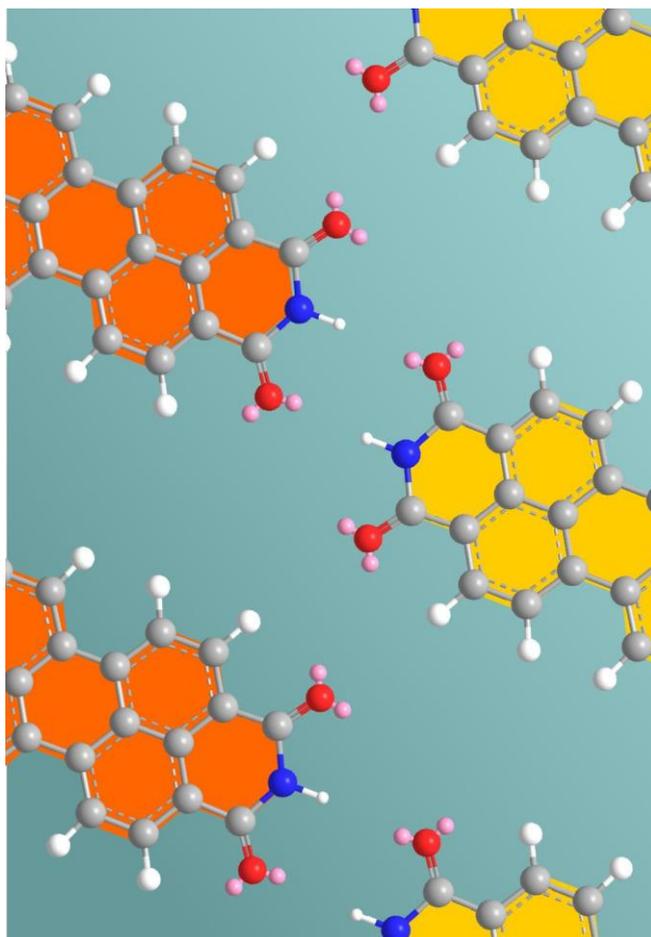


Figure S5. Illustration of the planar packing arrangement and formation of two types of hydrogen bonding, between aromatic proton and carbonyl as well as imide and carbonyl sites, of neighboring PDI **9** cores observed by SSNMR after annealing at 310 °C.

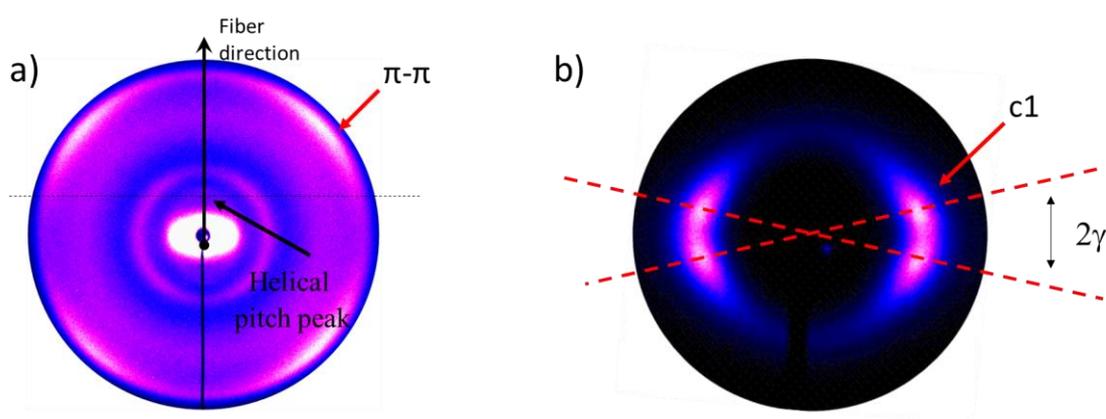


Figure S6. a) 2DWAXS pattern for PDI **9** annealed at 100 °C. Horizontal dashed line indicates the first scattering line to determinate the helical pitch. b) Magnification of the small angle range with indicated splitting of the intercolumnar reflections.

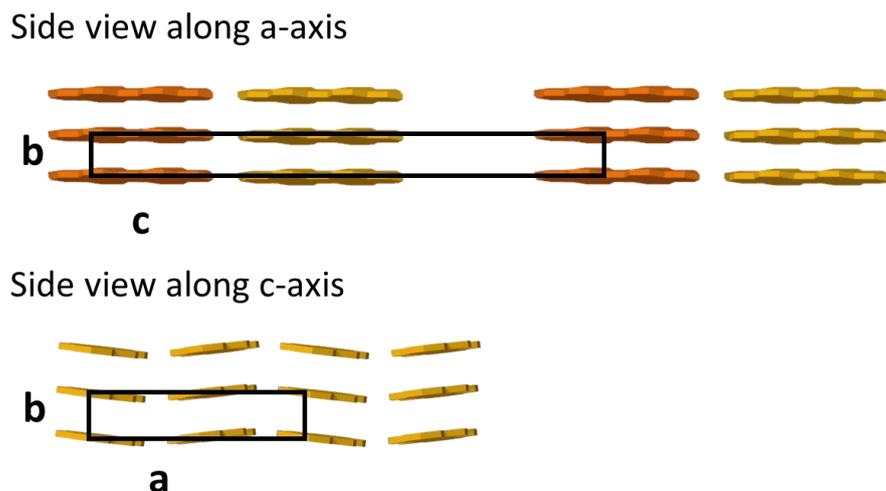


Figure S7. Model for the molecular arrangement of PDI **9** in the layer structure (side views) after annealing at 250 °C. Different colors are used to schematically visualize the molecular rotation. Side chains are omitted.

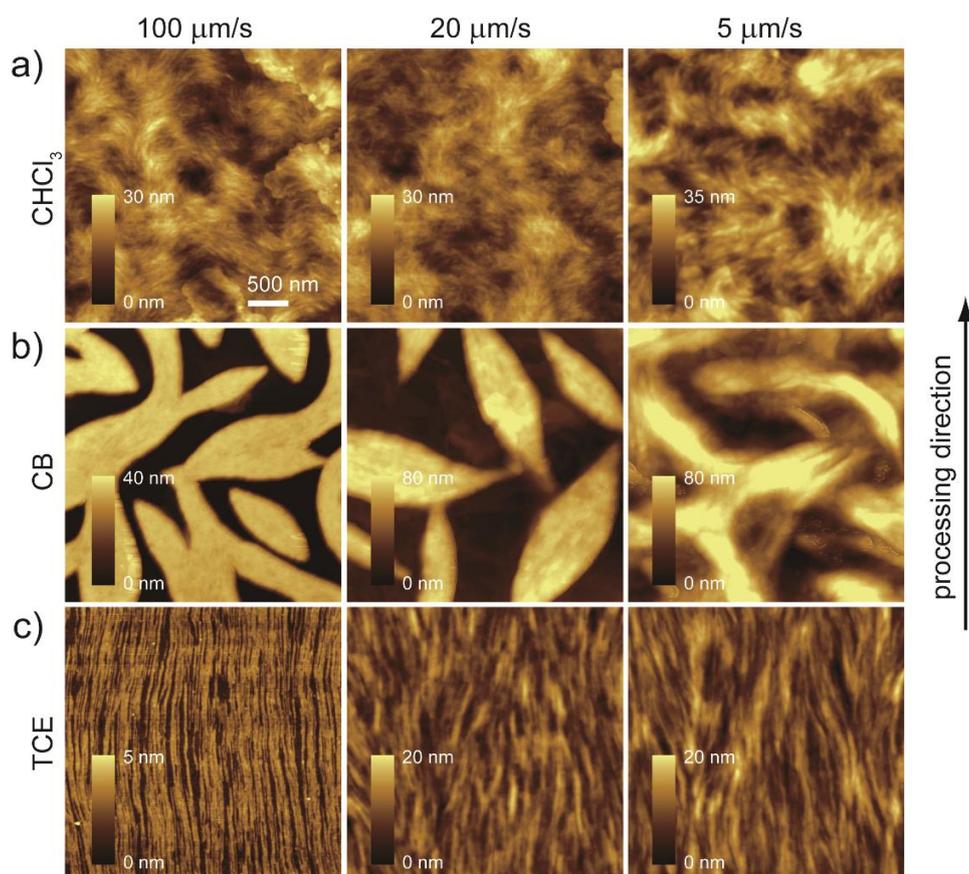


Figure S8. AFM height images of PDI **9** thin films processed by zone-casting with the concentration of 0.5 mg mL^{-1} . During zone-casting, the temperatures of solution/substrate are 50/40 °C, 78/82 °C and 70/60 °C for chloroform (CHCl_3), chlorobenzene (CB) and tetrachloroethane (TCE), respectively. All images have the same scale bars.