

Supporting Information

Aggregation Pathway Complexity in a Simple Perylene Diimide

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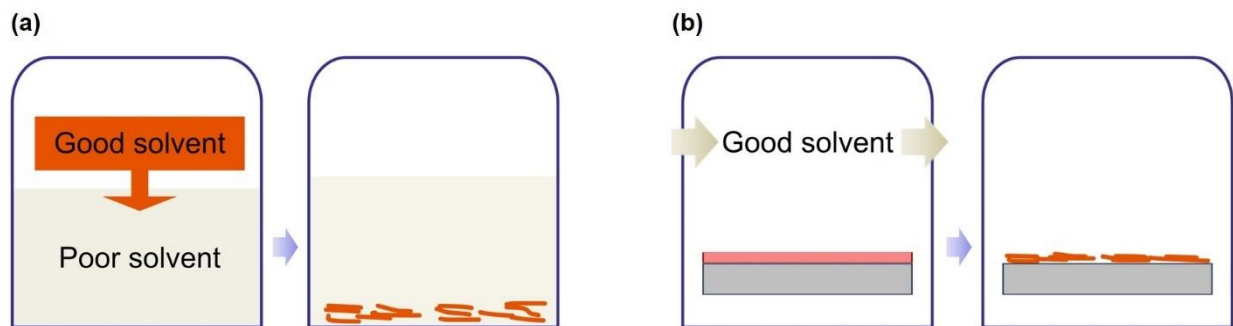


Figure S1. Fabrication processes for (a) solvent phase interfacial self-assembly (SPI) and (b) surface and solvent vapor assisted self-assembly (SSVA). In all images, orange represents presence of ddPDI, either as monomers (left in (a) and (b)) or aggregates (right in (a) and (b)).

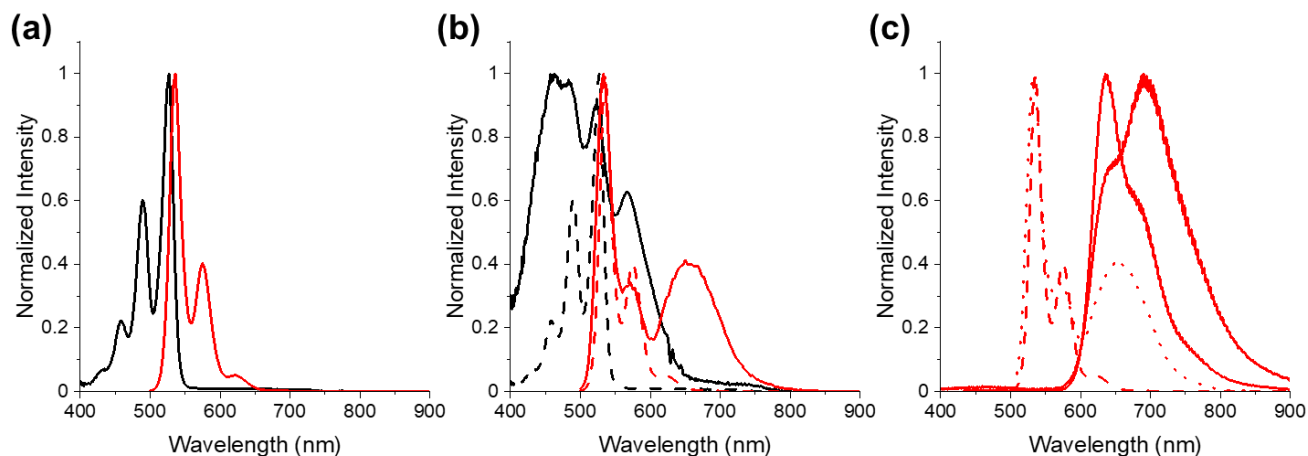


Figure S2. (a) Absorption (black) and fluorescence (red) spectra of 10 μ M ddPDI in chloroform. (b) Monomeric (dashed lines, also shown in (a)) and early aggregate (solid lines) absorption (black) and emission (red) spectra of ddPDI. (c) Fluorescence from ddPDI as monomers (dashed line, also shown in (a) and (b)), early aggregates (dotted line, also shown in (b)), and representative type 1 and type 2 ddPDI aggregates (solid lines), with aggregate spectra collected locally as also shown in Fig. 1f,g in the main text.

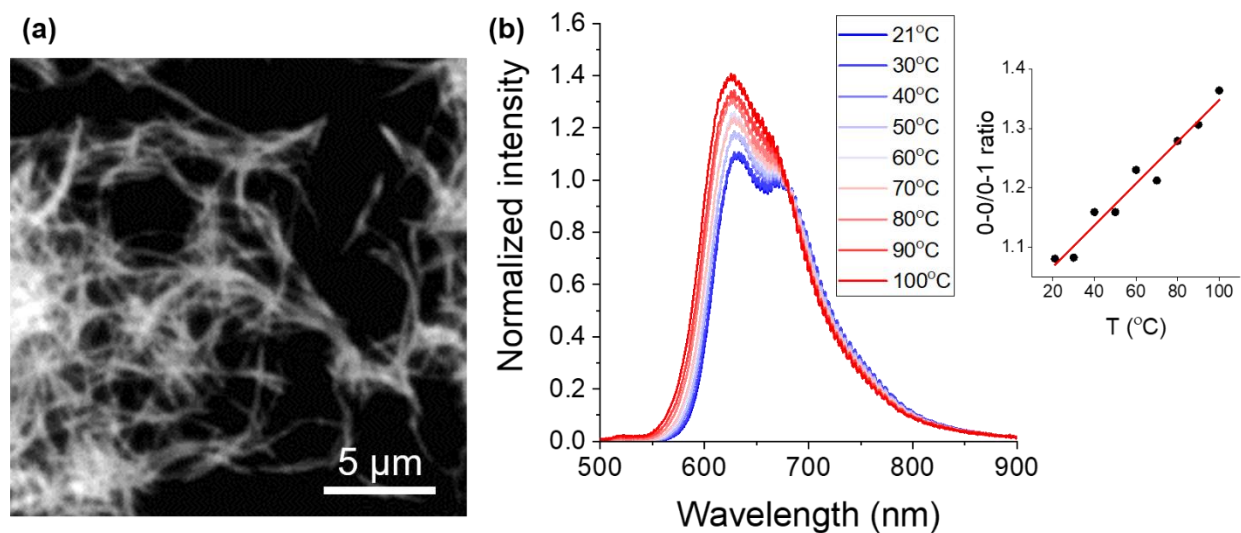


Figure S3. ddPDI aggregates prepared via SPI from a 10 μM ddPDI solution in a mixture of chloroform and methanol. (a) Representative fluorescence image and (b) temperature dependent-fluorescence spectra of ddPDI aggregates. Inset: Ratio of the 0-0/0-1 peak height and temperature as well as best-fit line to the data. Spectra were normalized to the 0-1 peak position at room temperature.

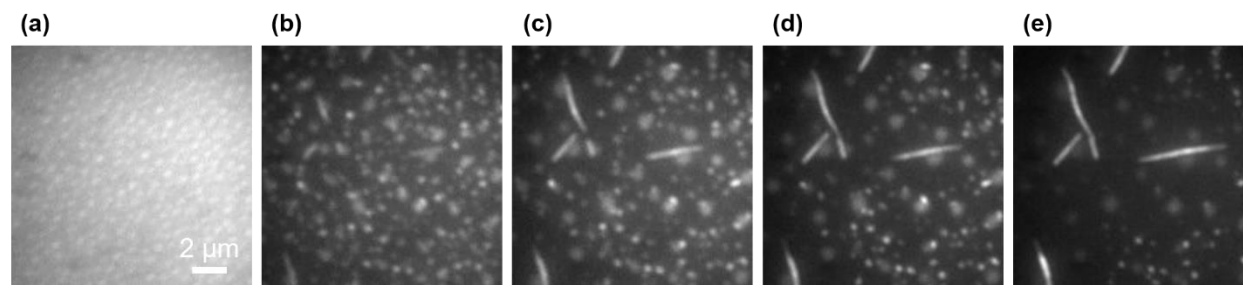


Figure S4. Early stages of the SSVA process. (a) Initial image, (b) image after 1, (c) 3, (d) 5, and (e) 10 minutes of delivering solvent. In (b-e) small ddPDI droplets and growing aggregates are visible. Location and scale is the same for all panels.

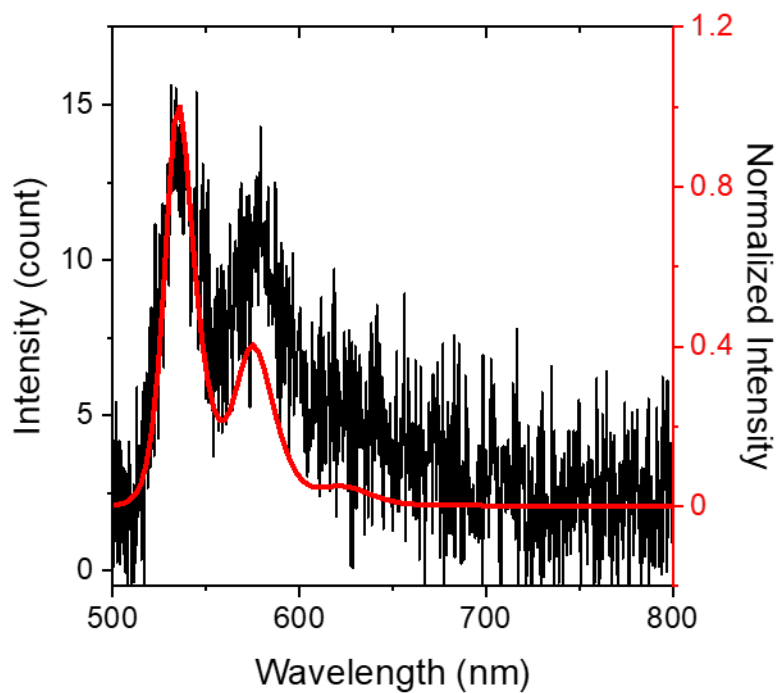


Figure S5. Comparison of emission spectra of (red) ddPDI monomers dissolved in chloroform and (black) residual ddPDI molecules from an area of the coverslip with no obvious aggregates. Red spectrum is also shown in Fig. S2 and black spectrum in Fig. 2b in the main text.

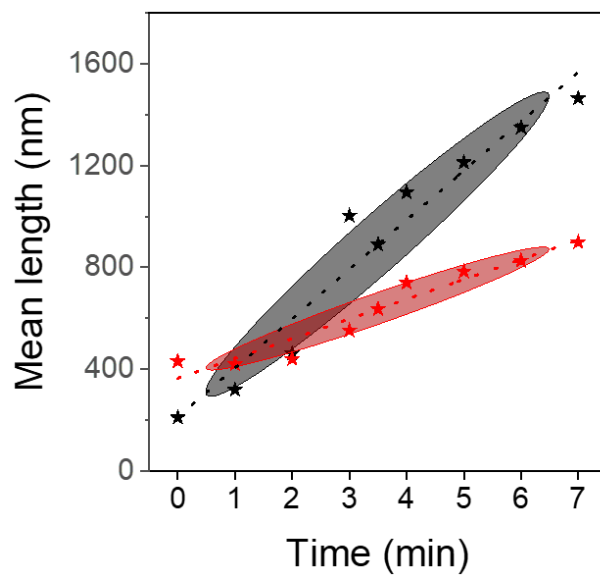


Figure S6. Growth of ddPDI aggregates prepared via a combined SSVA and SPI approach with SSVA only aggregates shown in black and seeded growth aggregates shown in red. Each data point represents the mean values of the FWHM of the measured length along the long axis of three aggregates in the same field of view. Dashed line is the best linear fit to each set of data. 2D ellipses represent the 95% confidence level of the fits.