

Electronic Supplementary Information

Perylene bisimide J-aggregates in polymer matrix: controlling self-assembly and fluorescence properties

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1. Materials and methods

Materials: Solvents and reagents were purchased from commercial sources, unless otherwise stated, and purified and dried according to standard procedures. The PBI **1** was synthesized and characterized according to the previous literature.^{S1} For all the samples before spin-coating, spectroscopy grade solvents were used without further purification. **PMMA** ($M_w = 120,000$ or $350,000$ g mol⁻¹), **PSt** ($M_w = 35,000$ g mol⁻¹), or **SBS** ($M_w = 140,000$ g mol⁻¹, polystyrene block: 30 wt%) were purchased from Sigma Aldrich. **PMMA** ($M_w = 15,000$ g mol⁻¹) was purchased from Acros Organics. **PMMA** ($M_w = 400,000$ g mol⁻¹) was purchased from Thermo Scientific. **PMMA** ($M_w = 800,000$ g mol⁻¹) was purchased from Tokyo Chemical Industry. All of the purchased polymers were used as received.

Spectroscopy and Microscopy: UV-Vis absorption spectra were measured on a Lambda 950 spectrophotometer equipped with an integrating sphere setup (Perkin-Elmer). Photoluminescence (PL) spectra were recorded on an Edinburgh Instruments FLS980-D2D2-ST spectrometer and were corrected against the photomultiplier sensitivity and the lamp intensity. Fluorescence lifetimes were determined with an EPL picosecond pulsed diode laser ($\lambda_{ex} = 479.7$ nm) for TCSPC with an Edinburgh Instruments FLS980-D2D2-ST spectrometer. The absolute photoluminescence quantum yield was determined on a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02. The system is composed of a 150 W CW Xenon lamp as the excitation source, a monochromator (250–700 nm, $FWHM = 10$ nm), an integrating sphere, and a multichannel spectrometer capable of simultaneously measuring multiple wavelengths between 300 and 900 nm. PL were determined using the absolute method without correction for reabsorption. AFM measurements were performed under ambient conditions using a Bruker AXS Multimode Nanoscope IV system operating in tapping mode in air. PL-POM measurements were performed under ambient conditions using a Zeiss Axio Imager optical polarization microscope equipped with an Ocean Optics Maya 2000Pro spectrometer.

Spin-coating Procedure: **1** and solid polymers (**PMMA**, **PSt**, or **SBS**) were dissolved in CHCl₃ by stirring for one hour at 40 °C and then 10 minutes sonication at room temperature. The solution was filtered with a polytetrafluoroethylene (PTFE) filter (0.22 μ m). Spin-coating was conducted at 1000 rpm for 30 seconds in one step after dropping 200 μ L of the CHCl₃ solution on glass substrates (20 mm * 20 mm, Boehringer Ingelheim Diagnostika GmbH).

Solvent Vapor Annealing: Spin-coated samples of **1**/polymer were placed in a small, closed chamber and a continuous flow of N₂ gas saturated with CHCl₃ vapor was applied for five minutes at room temperature. The samples were then dried at ambient condition before measurements.

Thermal Annealing: Spin-coated samples of **1**/polymer were placed on a precision heating stage (Harry Gestigkeit GmbH) set at 150 °C under ambient conditions and kept for 30 minutes. The samples were then cooled at ambient condition before measurements.

2. Effects of 1 concentration on absorption spectra

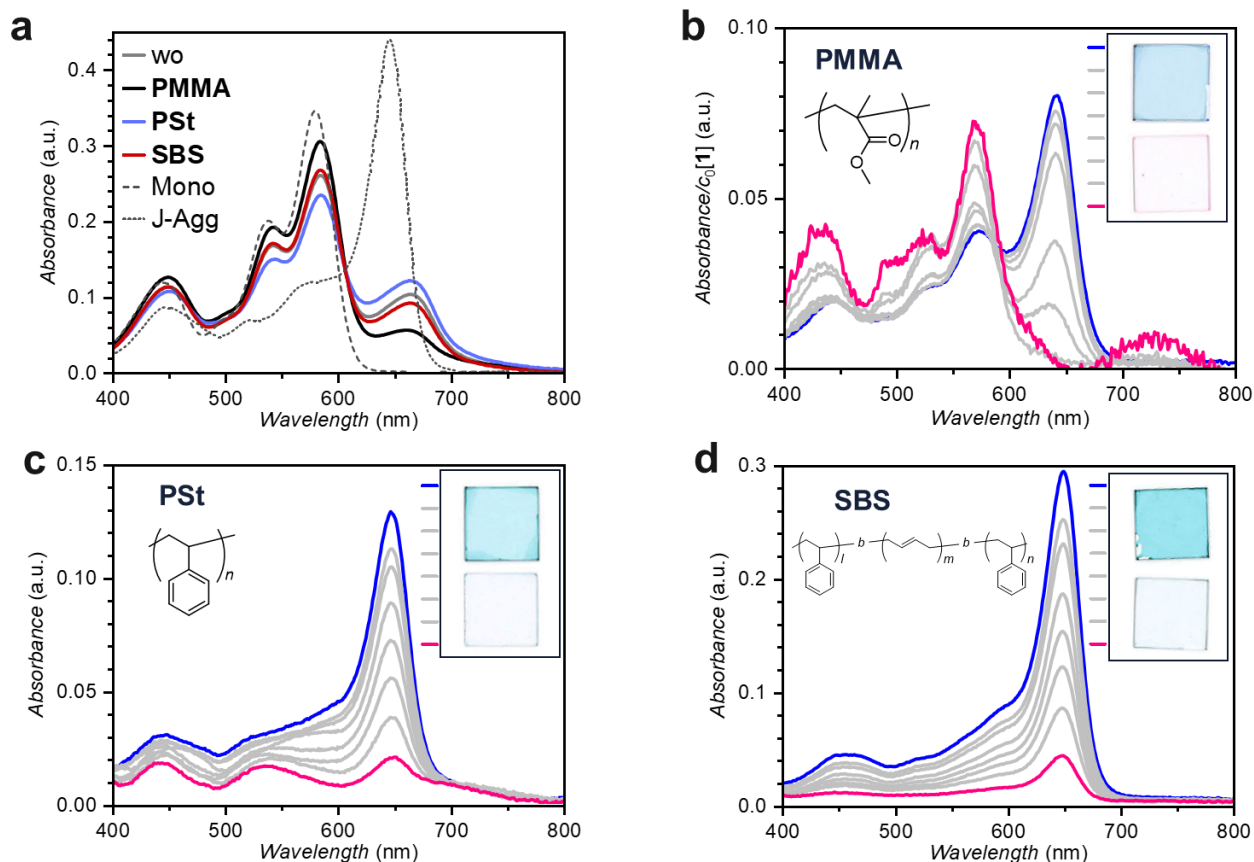


Figure S1. UV-Vis absorption spectra of (a) sample solutions in CHCl_3 ($c_0[\mathbf{1}] = 1.5 \text{ mg mL}^{-1}$, $c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) as well as (b-d) thin films prepared thereof on glass substrates. Scaled absorption spectra of PBI **1** in solution as monomer (dashed line; CH_2Cl_2) and J-aggregate (dotted line, methylcyclohexane) are provided in (a) as reference. Layers were obtained by spin-coating a CHCl_3 solution of polymers ((b) **PMMA**, (c) **PSt**, (d) **SBS**,) with different amount of **1** ($c_0[\mathbf{1}] = 0.2$ or 1.5 mg mL^{-1}). The insets in (b,c,d) display the photo scans of the respective layers ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$, $c_0[\mathbf{1}] = 0.2$ or 1.5 mg mL^{-1}). Note that the spectra in Figure S1b were scaled by dividing the UV-Vis absorption spectra through $c_0[\mathbf{1}]$ to access the degree of aggregation (approximation: volume of polymer layer independent of $c_0[\mathbf{1}]$).

3. Effects of polymer concentration on absorption spectra

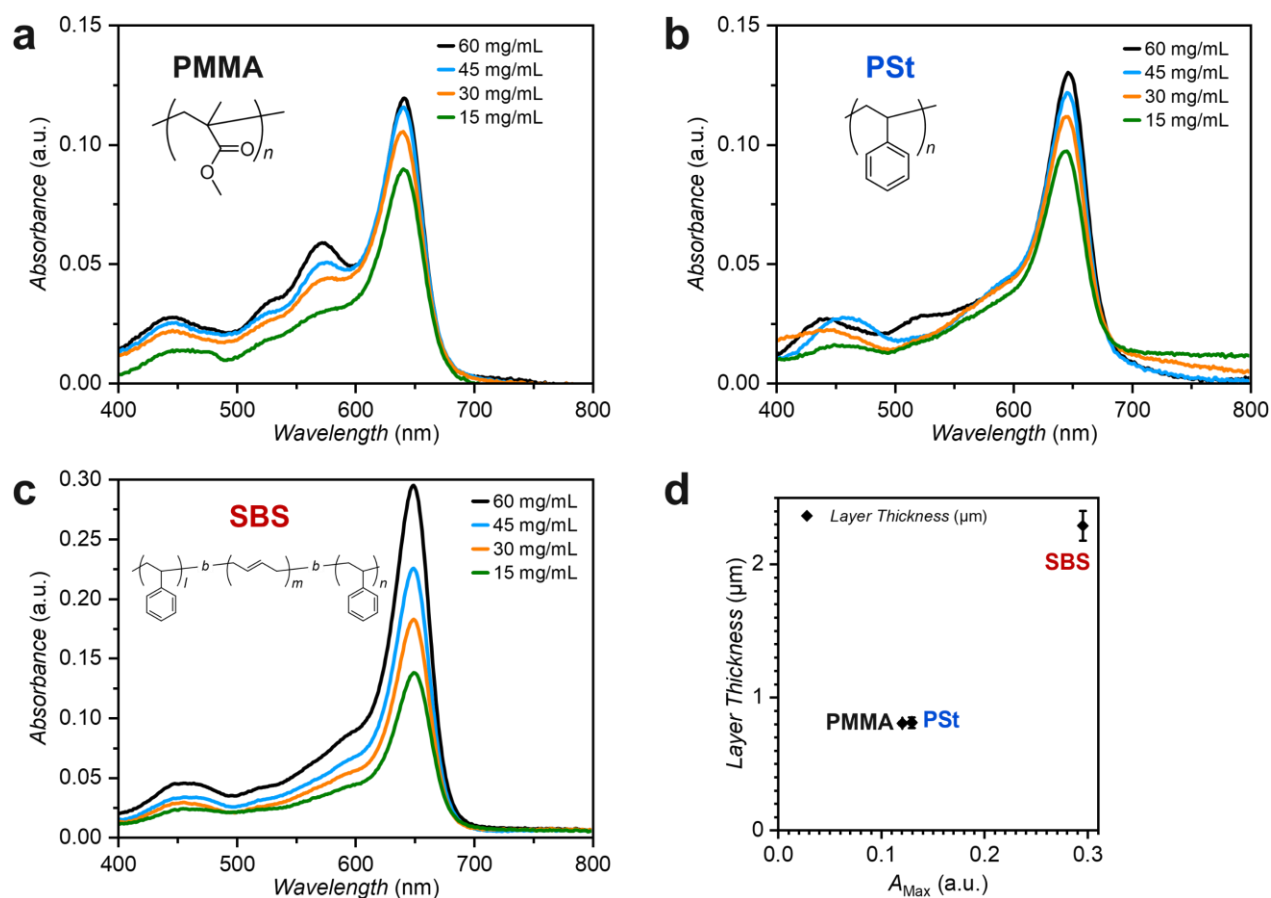


Figure S2. UV-Vis absorption spectra of thin films on glass substrates obtained by spin-coating a CHCl_3 solution of polymers ((a) **PMMA**, (b) **PSt**, (c) **SBS**, $c_0[\text{Polymer}] = 15, 30, 45$, or 60 mg mL^{-1}) with **1** ($c_0[\text{1}] = 1.5 \text{ mg mL}^{-1}$). (d) Plots of layer thickness of **1**/polymer matrix samples against the maximum absorbance of the matrices ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$).

4. Effects of polymer molecular weight on absorption spectra

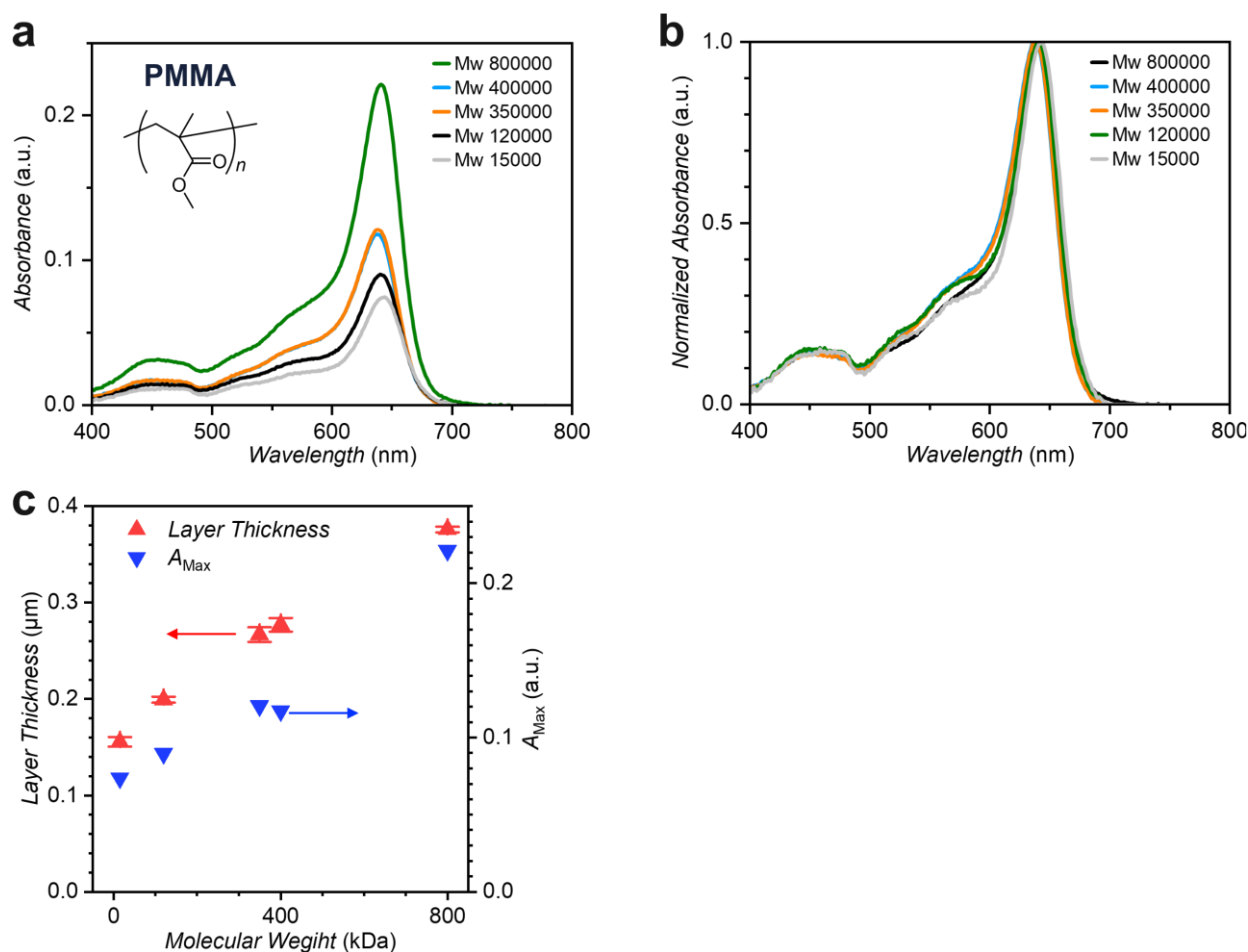


Figure S3. (a,b) UV-Vis absorption spectra of thin films on glass substrates obtained by spin-coating a CHCl_3 solution of **PMMA**, ($M_w = 15000, 120000, 350000, 400000$, and $800000 \text{ g mol}^{-1}$, $c_0[\text{Polymer}] = 15 \text{ mg mL}^{-1}$) with **1** ($c_0[\text{1}] = 1.5 \text{ mg mL}^{-1}$). Note that the spectra in (b) are normalized to enable a more easy comparison. (c) Plots of the layer thickness of **PMMA** matrices (blue triangle) and the absorbance of **1** at $\lambda_{\text{abs}} = 643 \text{ nm}$ in **PMMA** matrices (red reversed triangle) against the molecular weight (M_w). The layer thickness gets larger in accordance with molecular weight, and thus the absorbance also gets larger.

5. Absolute photoluminescence quantum yield of 1/polymer samples

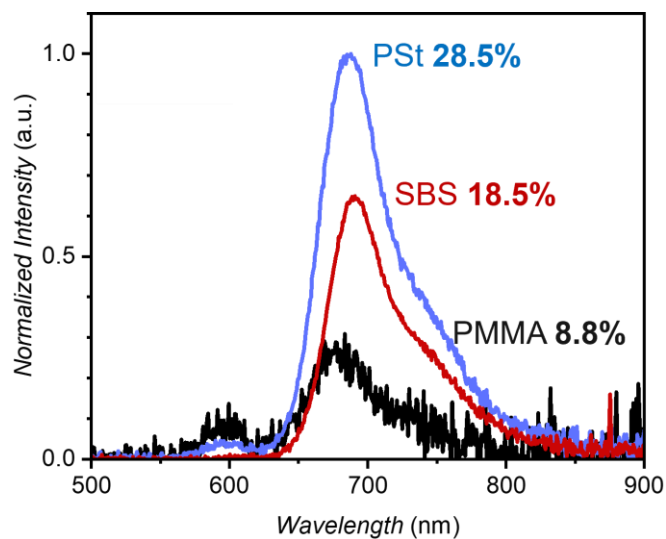


Figure S4. Emission spectra at $\lambda_{\text{exc}} = 445$ nm and the absolute quantum yield (Φ_{PL}) of **PMMA** (black), **PSt** (blue), or **SBS** (red) matrices with **1** J-aggregates on quartz substrates. Note that intensities are scaled to the respective Φ_{PL} of each sample.

6. Spectroscopic properties of the reference Ref-PBI

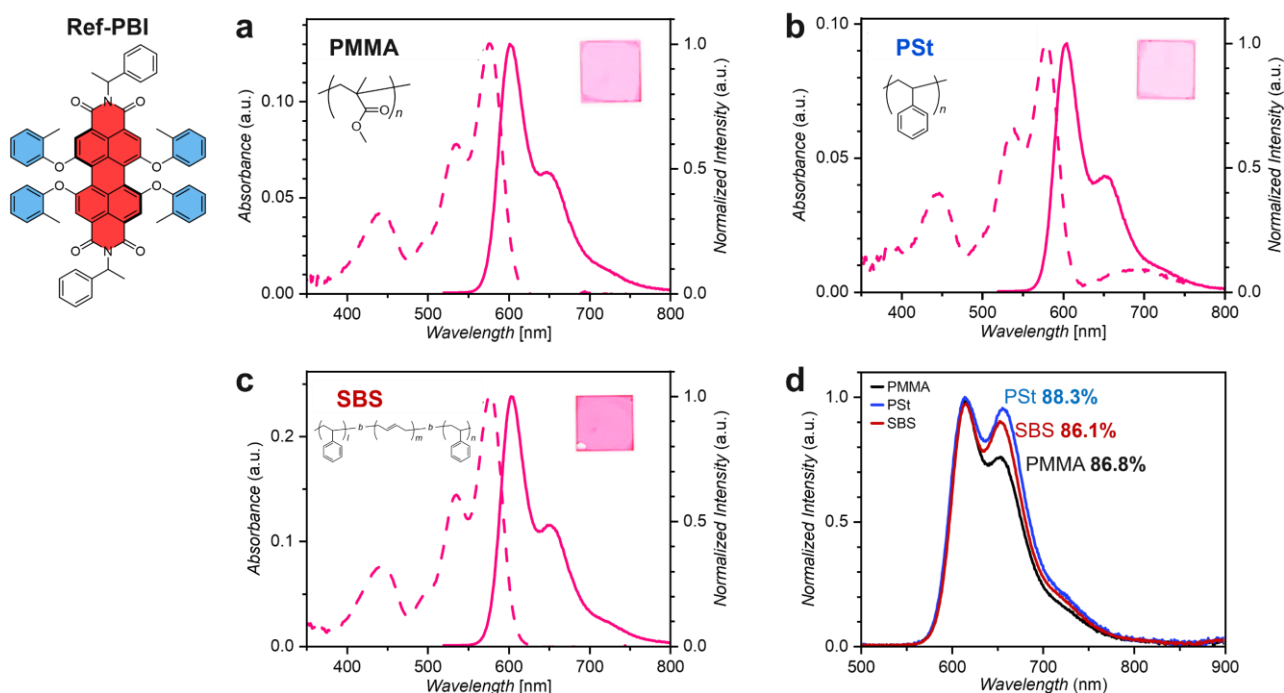


Figure S5. (a-c) UV-Vis absorption (dashed line) as well as respective emission (solid line) spectra of spin-coated polymer matrices ((a) **PMMA**, (b) **PSt**, (c) **SBS**, $c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with the reference PBI **Ref-PBI** ($c_0[\text{Ref-PBI}] = 1.5 \text{ mg mL}^{-1}$). The insets in (a,b,c) display the photo scans of the respective layers. (d) Emission spectra at $\lambda_{\text{exc}} = 445 \text{ nm}$ and the absolute Φ_{PL} of **PMMA** (black), **PSt** (blue), or **SBS** (red) matrices with **Ref-PBI** on quartz substrates ($c_0[\text{Ref-PBI}] = 1.5 \text{ mg mL}^{-1}$, $c_0(\text{Polymer}) = 60 \text{ mg mL}^{-1}$). Note that intensities are scaled to the respective Φ_{PL} of each sample.

Table S1. Spectroscopic Properties of Ref-PBI in Polymer Matrices

Polymer	$c_0[\text{Ref-PBI}]^a$	$c_0[\text{Polymer}]^a$	λ_{abs}	λ_{emi}^b	$FWHM^b$	Φ_{PLF}^c
	[mg mL ⁻¹]	[mg mL ⁻¹]	[nm]	[nm]	[cm ⁻¹]	[%]
PMMA	1.5	60	577	602	1210	86.8 ± 1.4
PSt	1.5	60	588	605	1080	88.3 ± 0.9
SBS	1.5	60	578	604	1100	86.1 ± 1.1

(a) Concentration of **Ref-PBI** and polymers in the CHCl₃ solutions before spin-coating. (b) $\lambda_{\text{exc}} = 460$ nm. (c) Absolute quantum yields measured with $\lambda_{\text{exc}} = 445$ nm.

7. Structural analysis on **1** J-aggregates in polymer matrices

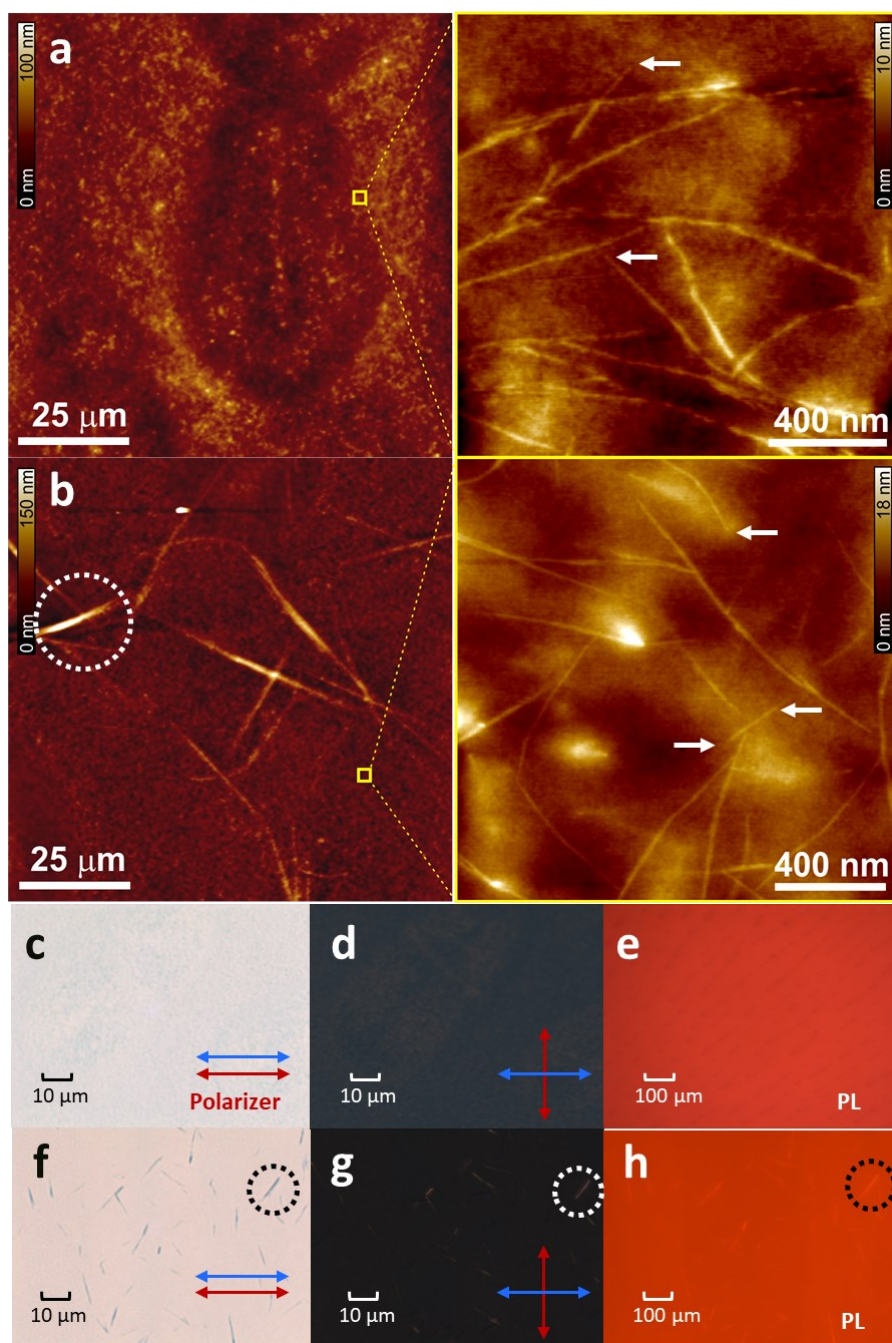


Figure S6. Structural analysis on **1** J-aggregates emerging from different polymer matrices. (a,b) AFM height as well as (c-h) respective PL- POM images of J-aggregates of **1** in (a,c-e) **PSSt**, and (b,f-h) **PMMA** matrix ($c_0[\mathbf{1}] = 1.5 \text{ mg mL}^{-1}$; $c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$). POM images were recorded in transmission mode with either parallel (c,f) or perpendicular (d,g) oriented polarizer and analyzer, while the PL-POM images were obtained in reflection mode under excitation with green light (e,h: $\lambda_{\text{exc}} = 530\text{-}580 \text{ nm}$). The dotted circles in (b,f-h) highlight a micrometer-sized crystal of **1** in the PMMA matrix, while the arrows in (a,b) indicate the permeation of J-aggregates of **1** through the polymer layers.

8. Effects of solvent vapor annealing on 1/PMMA samples

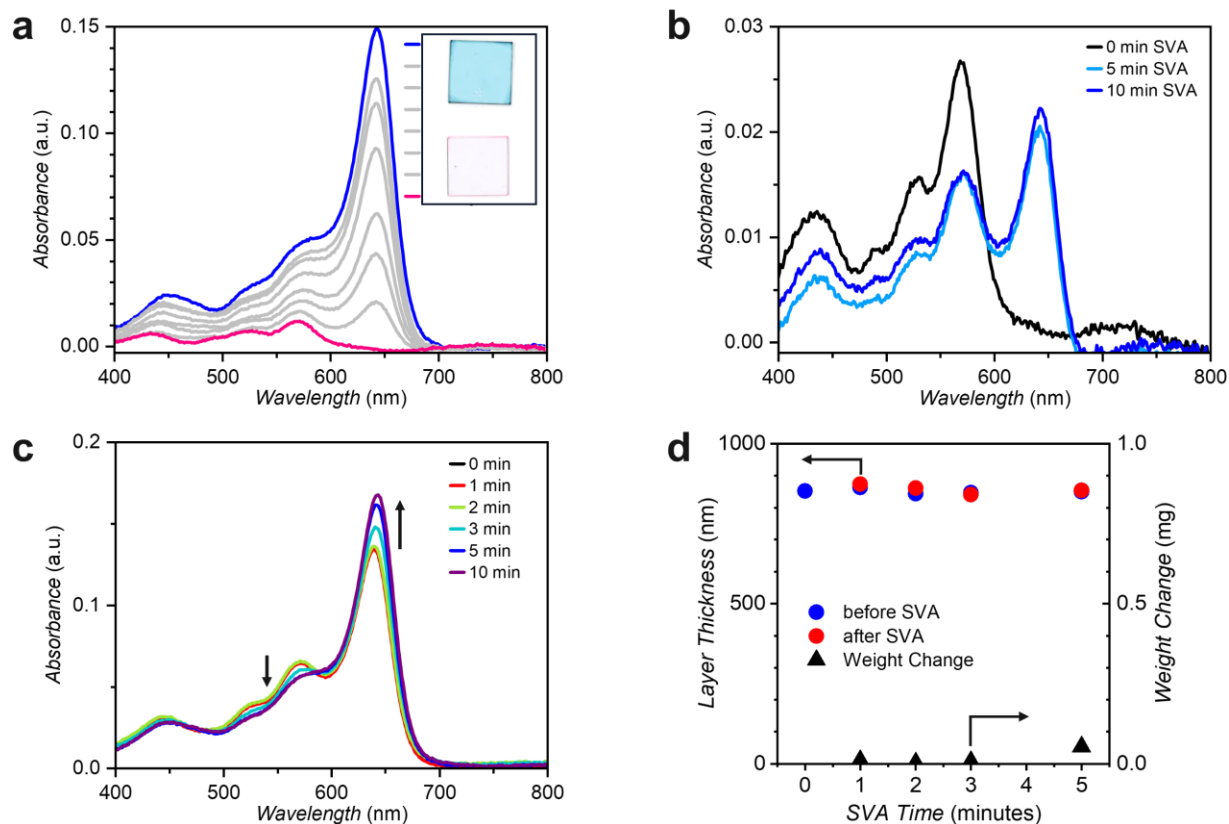


Figure S7. (a) UV-Vis absorption spectra of **PMMA** thin films ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with **1** ($c_0[1] = 0.2$ or 1.5 mg mL^{-1}) after solvent vapor annealing (SVA, CHCl_3 , 5 min). (b) UV-Vis absorption spectra of **PMMA** thin films ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with **1** ($c_0[1] = 0.4 \text{ mg mL}^{-1}$) before and after solvent vapor annealing (CHCl_3 , 5 or 10 min). (c) UV-Vis absorption spectra of **PMMA** thin films ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with **1** ($c_0[1] = 1.5 \text{ mg mL}^{-1}$) before and after solvent vapor annealing (CHCl_3 , 1 to 10 min). (d) Layer thickness and weight change of **PMMA** thin films ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with **1** ($c_0[1] = 1.5 \text{ mg mL}^{-1}$) before and after solvent vapor annealing (CHCl_3 , 1 to 10 min).

9. Effects of thermal annealing on 1/SBS samples

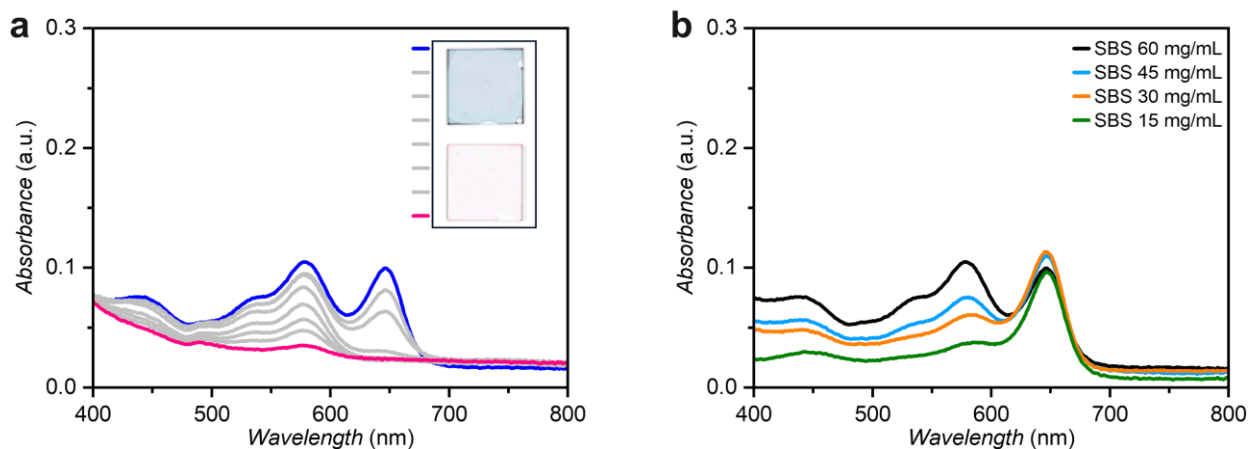


Figure S8. (a) UV-Vis absorption spectra of **SBS** thin films ($c_0[\text{Polymer}] = 60 \text{ mg mL}^{-1}$) with **1** ($c_0[\mathbf{1}] = 0.2$ or 1.5 mg mL^{-1}) after thermal annealing (ΔT : 150°C , 30 min). (b) UV-Vis absorption spectra of **SBS** thin films ($c_0[\text{Polymer}] = 15\text{-}60 \text{ mg mL}^{-1}$) with **1** ($c_0[\mathbf{1}] = 1.5 \text{ mg mL}^{-1}$) after ΔT (150°C , 30 min).

10. Effects of thermal annealing on 1/PSt sample

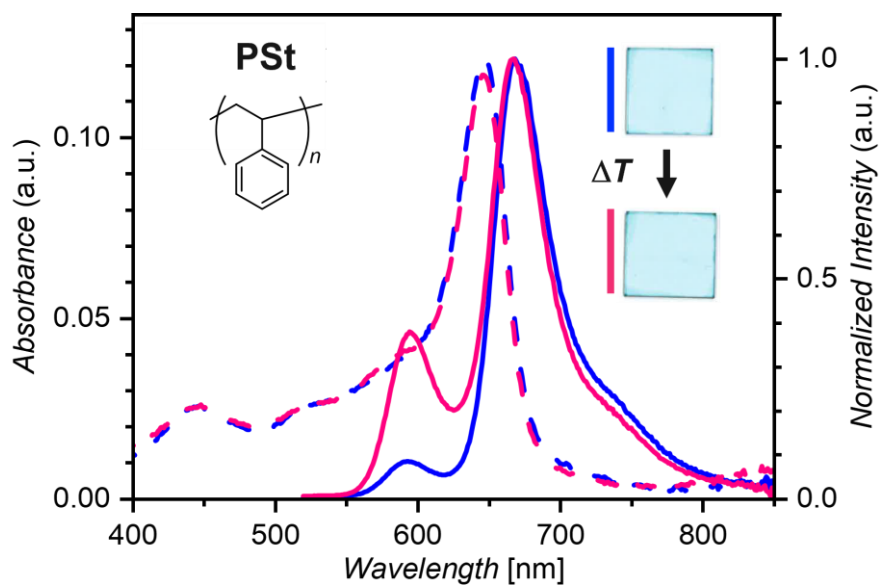


Figure S9. UV-Vis absorption (dashed line) and normalized emission (solid line, $\lambda_{\text{ex}} = 460$ nm) spectra of thin films of **1** in **PSt** thin film ($c_0[\mathbf{1}] = 1.5$ mg mL⁻¹, $c_0[\mathbf{PSt}] = 60$ mg mL⁻¹) before (blue) and after (red) ΔT (150 °C, 30 min).

11. Reference

(S1) Z. Xie, V. Stepanenko, B. Fimmel, F. Würthner, *Mater. Horiz.*, 2014, **1**, 355-359.