*Supporting Information for*

# Impact of Alkyl Spacer Length on Aggregation Pathways in Kinetically Controlled Supramolecular Polymerization

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KEYWORDS: Supramolecular polymer, Perylene bisimide, Off-pathway aggregate, Organogelator, Seeded polymerization

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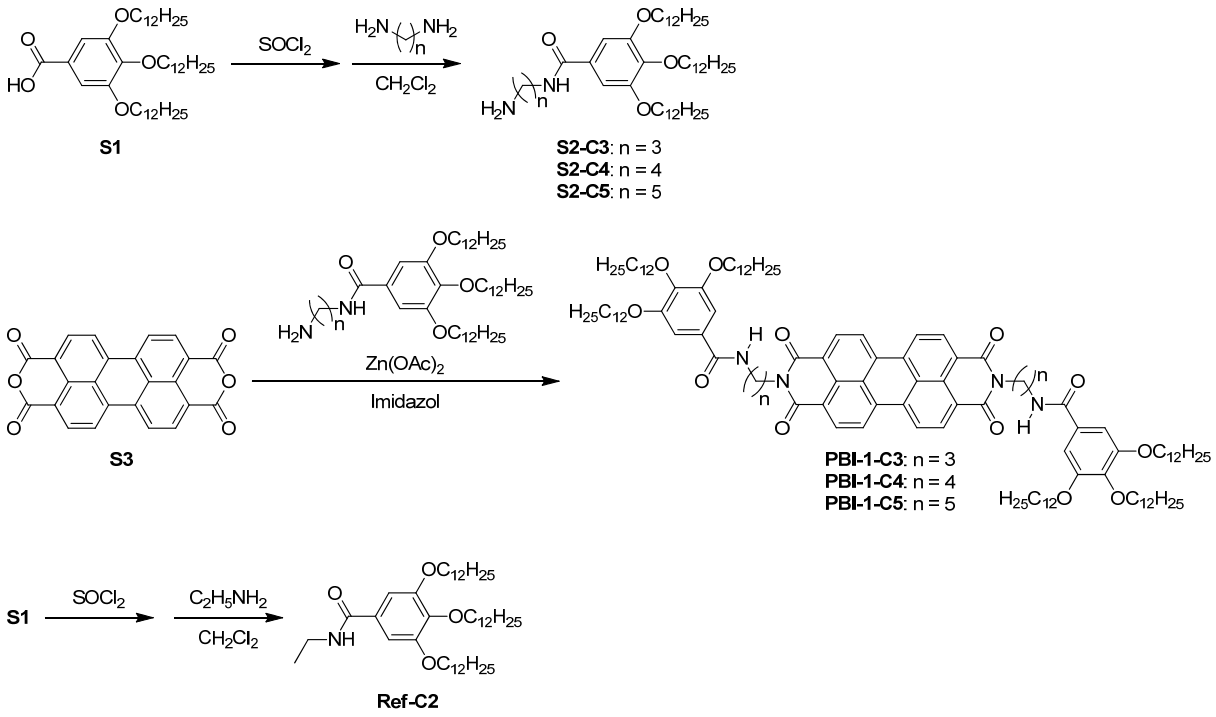
## 1. General

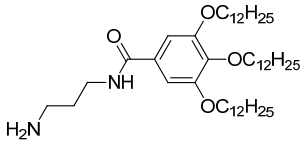
Solvents and reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Spectroscopic measurements were conducted under ambient conditions using dry solvents. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for $^{1}H$) or residual $CHCl_3$ (77 ppm for $^{13}C$) as the internal standard. UV/vis absorption spectra were recorded on a V-670 spectrophotometer equipped with a PAC-743R Auto Peltier 6/8-cell changer for temperature control. Atomic force microscopy (AFM) measurements were performed at ambient conditions with a Bruker AXS MultiMode$^{TM}$ 8 SPM system and Solver Next system from NT-MDT in semicontact mode. Silicon cantilevers (OMCL-AC160TS, Olympus) with a resonance frequency of ~300 kHz and spring constant of ~42 $Nm^{-1}$ were used. Scanning electron microscopy (SEM) measurements were performed with a Zeiss Ultra *plus* field emission scanning electron microscope. Images of the sample were taken using the SEM operated at 1.5 kV with an aperture size set to 30 μm to avoid excessive charging and radiation damage of the areas imaged. Fourier transform infrared (FT-IR) spectroscopic analysis was performed on a Jasco FT/IR-430 Spectrometer using a Beckmann Quick-mount IR Multicell Kit with KBr windows and path length of 1 mm. Molecular modeling calculations were performed by using the Gaussian 09 program package with B3-LYP as functional and def2-SVP as basis set. The structure was geometry optimized, followed by frequency calculation on the optimized structure, which confirmed the existence of a minimum.

## 2. Synthesis and characterization of PBI derivatives




**Scheme S1.** Synthesis routes of **PBI-1-C3**, **PBI-1-C4**, and **PBI-1-C5**, and the reference benzamide **ref-C2**.

**3,4,5-Tris(dodecyloxy)benzoic acid aminopropylamide** (**S2-C3**): A mixture of benzoic acid

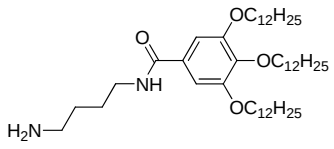


derivative **S1** (300 mg, 0.44 mmol), which was synthesized according to a reported method,[S1] and thionyl chloride (1 mL) was stirred at 85 °C for 2 h under $N_2$. After the thionyl chloride was distilled at 50 °C under vacuum, the crude product was obtained as a white solid and it was taken to the next step without further purification. It was redissolved in dry dichloromethane (5 mL) and the solution was slowly added dropwise to an ice-cold flask containing a solution of 1,3-diaminopropane (330 mg, 4.44 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred in the same ice bath for another 1 h. Then the solvent was evaporated in

the presence of $SiO_2$ (15 g). The solid residue was purified through column chromatography ($SiO_2$; DCM/MeOH, 85:15 in volume; $\phi$ 3 cm × 6 cm) to yield **S2-C3** as a light yellow solid (97%).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 7.55 (t, 1 H, $J$ = 5.1 Hz, NH), 6.99 (s, 2 H, Ar-H), 4.04-3.91 (m, 6H, Ar-$OCH_2$), 3.59-3.50 (m, 2H, $CH_2$), 2.90 (t, 2H, $J$ = 6.0 Hz, $CH_2$), 1.84-1.67 (m, 8H, $CH_2$), 1.51-1.39 (m, 6H, $CH_2$), 1.39-1.16 (m, 50H, $CH_2$), 0.87 (t, 9H, $J$ = 6.9 Hz, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 167.17, 152.93, 140.84, 129.64, 105.61, 73.44, 69.22, 40.73, 39.33, 31.91, 31.90, 31.45, 30.27, 29.72, 29.71, 29.70, 29.68, 29.63, 29.62, 29.56, 29.38, 29.37, 29.34, 29.32, 26.06, 22.66, 14.09, 0.98; HRMS (ESI): $m/z$ calcd for $C_{46}H_{87}N_2O_4$ $[M+H]^+$: 731.6666; found: 731.6666.

**3,4,5-Tris(dodecyloxy)benzoic acid aminobutylamide** (**S2-C4**): Compound **S2-C4** was

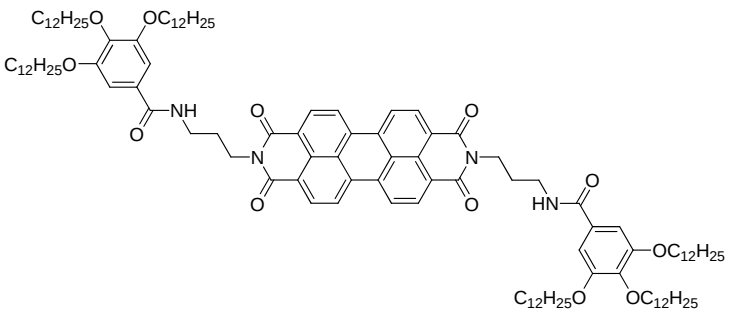



synthesized according to the above-described procedure for compound **S2-C3** using benzoic acid derivative **S1** (250 mg, 0.37 mmol), thionyl chloride (1 mL), 1,4-diaminobutane (260 mg, 2.95 mmol), and dry dichloromethane (15 mL). Light yellow solid (36%); $^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 6.96 (s, 2 H, Ar-H), 6.69 (br, 1 H, NH), 4.04-3.94 (m, 6H, Ar-$OCH_2$), 3.50-3.40 (m, 2H, $CH_2$), 2.81-2.72 (m, 2H, $CH_2$), 1.88-1.16 (m, 64H, $CH_2$), 1.16-1.04 (br, 2H, $NH_2$), 0.88 (t, 9H, $J$ = 6.9 Hz, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 167.29, 153.01, 140.96, 129.76, 105.66, 73.47, 69.33, 41.55, 41.43, 40.01, 39.88, 31.93, 31.92, 30.80, 30.76, 30.29, 29.73, 29.72, 29.69, 29.65, 29.64, 29.58, 29.40, 29.36, 27.07, 26.07, 22.69, 14.12; HRMS (ESI): $m/z$ calcd for $C_{47}H_{89}N_2O_4$ $[M+H]^+$: 745.6822; found: 745.6819.

**3,4,5-Tris(dodecyloxy)benzoic acid aminopentylamide** (**S2-C5**): Compound **S2-C5** was synthesized according to the above-described procedure for compound **S2-C3** using benzoic acid derivative **S1** (250 mg, 0.37 mmol), thionyl chloride (1 mL), 1,5-diaminopentane (378 mg, 3.70 mmol), and dry dichloromethane (15 mL). Light yellow solid (95%); $^{1}$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 7.22 (br, 1 H, NH), 7.05 (s, 2 H, Ar-H), 4.00-3.84 (m, 6H, Ar-$OCH_2$), 3.40-3.26 (m, 2H, $CH_2$), 2.97 (m, 2H, $CH_2$), 1.84-1.65 (m, 8H, $CH_2$), 1.65-1.51 (m, 2H, $CH_2$), 1.51-1.35 (m, 8H, $CH_2$), 1.35- 1.16 (m, 57H, $CH_2$, $CH_3$), 0.87 (t, 9H, $J$ = 6.9 Hz, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 167.57, 152.95, 140.84, 129.03, 105.63, 73.44, 69.17, 53.40, 39.81, 31.92, 30.35, 29.76, 29.74, 29.69, 29.64, 29.51, 29.38, 28.86, 27.03, 26.17, 26.10, 23.70, 22.68, 14.09; HRMS (ESI): $m/z$ calcd for $C_{48}H_{91}N_2O_4$ $[M+H]^+$: 759.6979; found: 759.6982.

**3,4,5-Tris(dodecyloxy)benzethylamide** (**ref-C2**): Compound **ref-C2** was synthesized according to the above-described procedure for compound **S2-C3** using benzoic acid derivative **S1** (250 mg, 0.37 mmol), thionyl chloride (1 mL), 2M ethylamine in tetrahydrofuran (280 μL), and dry dichloromethane (10 mL). Light yellow solid (93%); $^{1}$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 6.94 (s, 2 H, Ar-H), 5.97 (t, 1 H, $J$ = 5.4 Hz, NH), 4.05-3.94 (m, 6H, Ar-$OCH_2$), 3.53-3.42 (m, 2H, $CH_2$), 1.85-1.68 (m, 6H, $CH_2$), 1.52-1.40 (m, 6H, $CH_2$), 1.40-1.20 (m, 51H, $CH_2$, $CH_3$), 0.88 (t, 9H, $J$ = 6.9 Hz, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 167.35, 153.05, 140.99, 129.80, 105.56, 73.48, 69.34, 34.98, 31.93, 31.92, 30.29, 29.73, 29.69, 29.65, 29.63, 29.57, 29.39, 29.36, 26.06, 22.69, 14.94, 14.12; HRMS (ESI): $m/z$ calcd for $C_{45}H_{84}NO_4$ $[M+H]^+$: 702.6400; found: 702.6397.

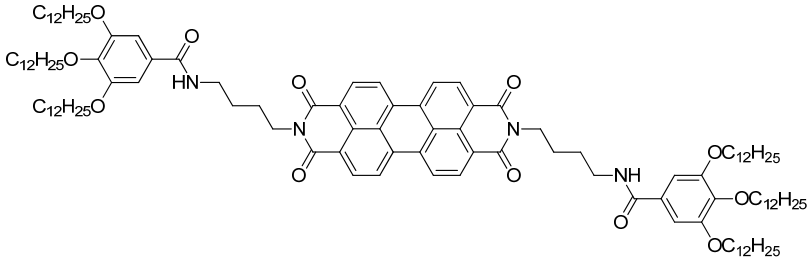
***N,N'*-Di[3,4,5-tris(dodecyloxy)benzoylaminoethyl]-perylene-3,4:9,10-tetracarboxylic**



**acid bisimide** (**PBI-1-C3**): Perylene-3,4:9,10-tetracarboxylic acid bisanhydride (73 mg, 0.19 mmol), benzamide **S2-C3** (300 mg, 0.41 mmol) and zinc acetate (137 mg, 0.74 mmol) were mixed in 3 g of imidazole. The reaction mixture was stirred at 100 °C for 6 h. After cooling to room temperature, the mixture was extracted with $CHCl_3$ (50 mL) and the organic layer was washed with 1N HCl (twice). The filtrate was dried in vacuum and the crude product was purified by preparative TLC ($SiO_2$; $CHCl_3$/aceton, 98:2 in volume) to give a red solid (75%).

$^1$H NMR (400 MHz, CDCl3, 300 K): $\delta$ = 8.74-8.67 (m, 8H, H-pery), 7.30 (t, 2H, $J$ = 6.1 Hz, NH), 7.18 (s, 4H, Ar-H), 4.38 (t, 4H, $J$ = 6.1 Hz, $CH_2$), 4.10 (t, 8H, $J$ = 6.6 Hz, Ar-$OCH_2$), 4.01 (t, 4H, $J$ = 6.5 Hz, Ar-$OCH_2$), 3.48 (q, 4H, $J$ = 5.8 Hz, $CH_2$), 2.15-2.09 (m, 4H, $CH_2$), 1.88-1.72 (m, 12H, $CH_2$), 1.53-1.14 (m, 108H, $CH_2$), 0.91-0.81 (m, 18H, $CH_3$); HRMS (ESI): $m/z$ calcd for $C_{116}H_{177}N_4O_{12}$ $[M+H]^+$: 1819.3397; found: 1819.3404; elemental analysis (%) calculated for $C_{116}H_{176}N_4O_{12}$ (1818.7): C 76.61, H 9.75, N 3.08; found: C 76.23, H 9.62, N 2.82.

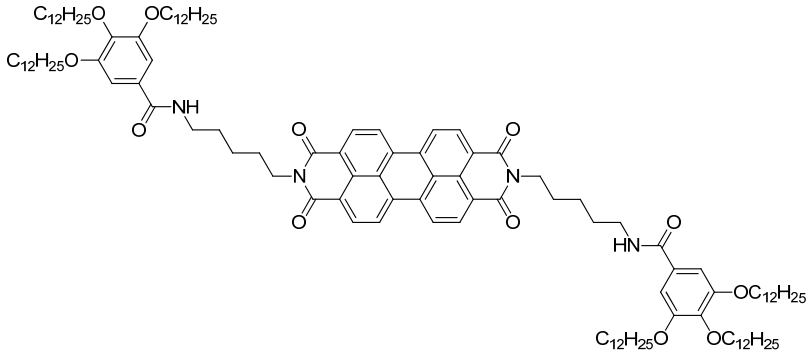
***N,N'*-Di[3,4,5-tris(dodecyloxy)benzoylaminopropyl]-perylene-3,4:9,10-tetracarboxylic**



**acid bisimide** (**PBI-1-C4**): Compound **PBI-1-C4** was synthesized according to the above-described procedure for compound **PBI-1-C3** using perylene-3,4:9,10-tetracarboxylic acid bisanhydride (23 mg,

0.06 mmol), benzamide **S2-C4** (96 mg, 0.13 mmol), zinc acetate (43 mg, 0.23 mmol), and imidazole (2 g). Red solid (76%); $^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 8.65 (d, 4H, $J$ = 8.0 Hz, H-pery), 8.58 (d, 4H, $J$ = 8.2 Hz, H-pery), 7.04 (s, 4H, Ar-H), 6.57 (t, 2H, $J$ = 5.7 Hz, NH), 4.26 (t, 4H, $J$ = 7.2 Hz, $CH_2$), 4.06-3.92 (m, 12H, Ar-$OCH_2$), 3.58 (q, 4H, $J$ = 6.4 Hz, $CH_2$), 1.97-1.85 (m, 4H, $CH_2$), 1.85-1.67 (m, 16H, $CH_2$), 1.50-1.38 (m, 12H, $CH_2$), 1.35-1.19 (m, 96H, $CH_2$), 0.92-0.81 (m, 18H, $CH_3$); HRMS (ESI): $m/z$ calcd for $C_{118}H_{181}N_4O_{12}$ $[M+H]^+$: 1847.3710; found: 1847.3690.

***N*,*N*'-Di[3,4,5-tris(dodecyloxy)benzoylaminobutyl]-perylene-3,4:9,10-tetracarboxylic acid bisimide** (**PBI-1-C5**): Compound **PBI-1-C5** was synthesized according to the above-described procedure for compound **PBI-1-C3** using perylene-3,4:9,10-tetracarboxylic acid bisanhydride (35 mg, 0.09 mmol), benzamide **S2-C5** (150 mg, 0.20 mmol), zinc acetate (66 mg, 0.36 mmol), and imidazole (3 g). Red solid (75%); $^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 8.64-8.51 (m, 8H, H-pery), 6.95 (s, 4H, Ar-H), 6.24 (t, 2H, $J$ = 5.5 Hz, NH), 4.25 (t, 4H, $J$ = 7.1 Hz, $CH_2$), 4.03-3.93 (m, 12H, Ar-$OCH_2$), 3.48 (q, 4H, $J$ = 6.3 Hz, $CH_2$), 1.90-1.70 (m, 20H, $CH_2$), 1.53-1.18 (m, 112H, $CH_2$), 0.90-0.84 (m, 18H, $CH_3$); HRMS (ESI): $m/z$ calcd for $C_{120}H_{185}N_4O_{12}$ $[M+H]^+$: 1875.4023; found: 1875.4008.



### 3. $^1$H NMR spectra of monomeric ref-C2 and PBI-1-C4

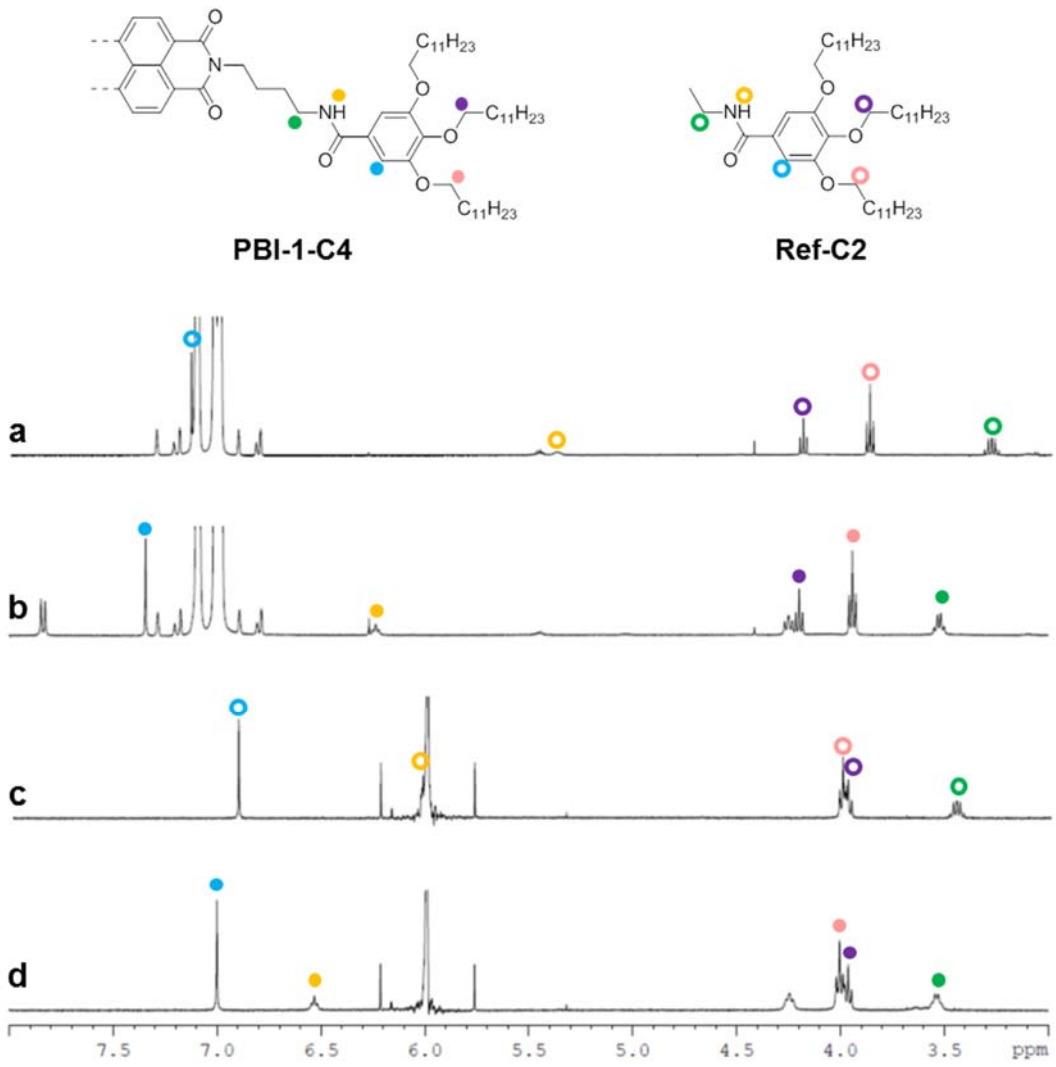



**Figure S1.** Partial $^1$H NMR spectra of (a) **ref-C2** and (b) **PBI-1-C4** in toluene-$d_8$ ($c_T$ = 2.5 × $10^{-4}$ M, 338 K) and (c) **ref-C2** and (d) **PBI-1-C4** in 1,1,2,2-tetrachloroethane-$d_2$ ($c_T$ = 5 × $10^{-4}$ M, 298 K). Chemical shifts of each proton peak are provided in the Supporting Information Tables S1 and S2.

Interpretation: In 1,1,2,2-tetrachloroethane-$d_2$ the amide N–H proton peak of monomeric **PBI-1-C4** was observed at 6.53 ppm, which is downfield-shifted by 0.52 ppm compared with that of **ref-C2**. This downfield shift is rationalized by a small fraction of intramolecularly hydrogen-bonded molecules. In less polar toluene-$d_8$ this fraction is increased and accordingly the difference in the chemical shift ($\Delta\delta$) of the amide N–H proton becomes larger (0.88 ppm). Additionally, downfield shifts are observable for proton peaks of the butylene spacer and trialkoxyphenyl group in particular in toluene-$d_8$. These downfield shifts can also be

rationalized by the formation of intramolecular hydrogen bonds between the amide hydrogens and imide carbonyl oxygens, leading to a conformation (see Supporting Information Figure S2c) where the ring current effect of the PBI is exerted on the butylene and trialkoxyphenyl protons.

**Table S1.** Chemical shifts of amide N–H proton and trialkoxyphenyl protons of **PBI-1-C4** and **ref-C2** in 1,1,2,2-tetrachloroethane-$d_2$ ($c_T = 5 \times 10^{-4}$ M, 298 K) and the difference in the chemical shift ($\Delta\delta$) of each proton peak of **PBI-1-C4** and **ref-C2**.

| | Chemical shifts of **PBI-1-C4** (ppm) | Chemical shifts of **ref-C2** (ppm) | $\Delta\delta$ (ppm) |
|---|---|---|---|
| amide N-*H* | 6.53 | 6.01 | 0.52 |
| OC*H*$_2$ (*p*-position) | 3.96 | 3.96 | 0 |
| OC*H*$_2$ (*o*-position) | 4.00 | 3.99 | 0.01 |
| Phenyl proton | 7.00 | 6.90 | 0.10 |
| C*H*$_2$NH | 3.54 | 3.44 | 0.10 |

**Table S2.** Chemical shifts of amide N–H proton and trialkoxyphenyl protons of **PBI-1-C4** and **ref-C2** in toluene-$d_8$ ($c_T = 2.5 \times 10^{-4}$ M, 338 K) and the difference in the chemical shift ($\Delta\delta$) of each proton peak of **PBI-1-C4** and **ref-C2**.

| | Chemical shifts of **PBI-1-C4** (ppm) | Chemical shifts of **ref-C2** (ppm) | $\Delta\delta$ (ppm) |
|---|---|---|---|
| amide N-*H* | 6.24 | 5.36 | 0.88 |
| OC*H*$_2$ (*p*-position) | 4.20 | 4.18 | 0.02 |
| OC*H*$_2$ (*o*-position) | 3.94 | 3.86 | 0.08 |
| Phenyl proton | 7.34 | 7.12 | 0.22 |
| C*H*$_2$NH | 3.52 | 3.27 | 0.25 |

## 4. Energy minimized structures of PBI derivatives

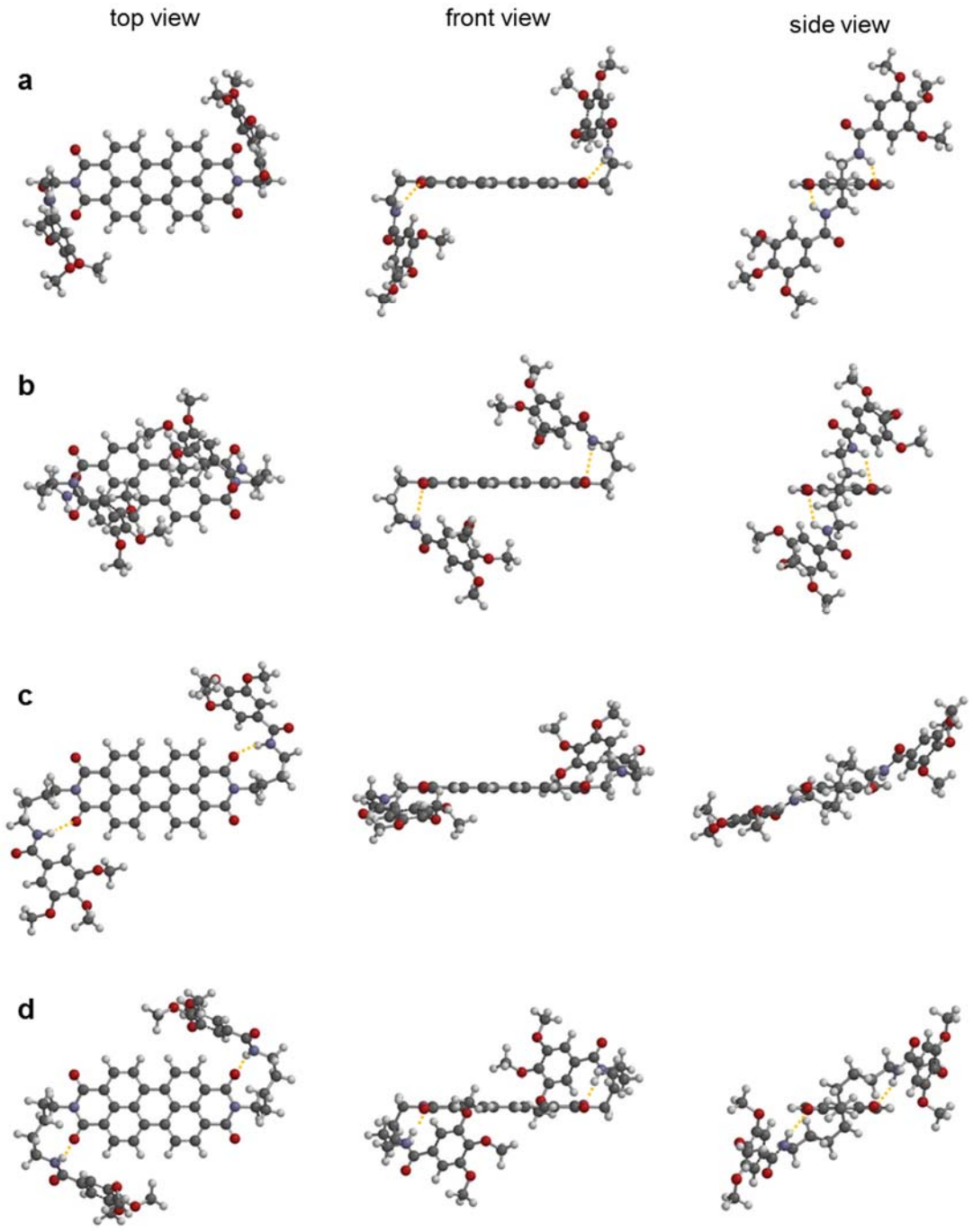



**Figure S2.** (a-d) Energy minimized structures obtained from DFT calculations (Gaussian 09 program package with B3-LYP as functional and def2-SVP as basis set) of (a) **PBI-1-C2**, (b) **PBI-1-C3**, (c) **PBI-1-C4**, and (d) **PBI-1-C5**. Trisdodecyloxy groups are replaced by trimethoxy groups for simplicity. The dashed orange lines represent intramolecular hydrogen bonds.

## 5. Analysis of self-assembly behavior of PBI-1-C4

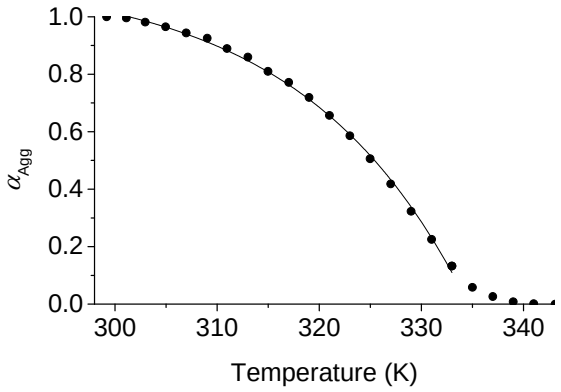



**Figure S3.** Temperature-dependent degree of aggregation ($\alpha_{Agg}$) for **PBI-1-C4$_{Agg1}$** calculated from the apparent absorption coefficients at $\lambda$ = 523 nm at a total concentration of $c_T$ = 5 × $10^{-6}$ M in MCH/toluene (2:1, v/v). The curve shows the resulting fit of the elongation regime calculated according to the cooperative model proposed by Meijer and co-workers.[S2,S3]

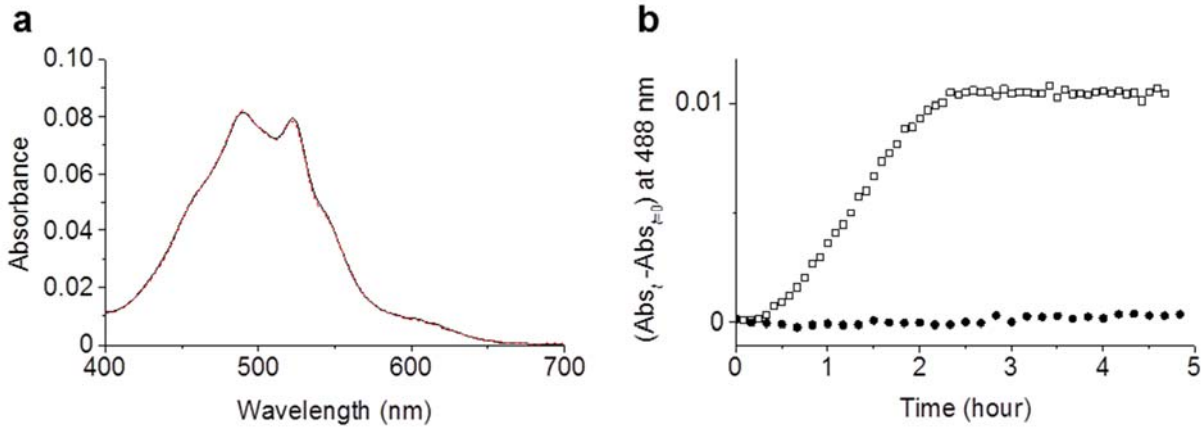



**Figure S4.** (a) Absorption spectra of an unstirred solution of **PBI-1-C4$_{Agg1}$** in MCH/toluene (2:1, v/v) observed 0 (black solid line) and 5 h (red dotted line) after rapid cooling from 353 to 308 K. Conditions: $c_T$ = 5 × $10^{-6}$ M, 308 K. (b) Time-dependent absorbance changes at 488 nm of the unstirred solution (closed circles) observed in Figure S4a and the solution under stirring at a rate of 400 rpm (open squares) observed in Figure 5a.

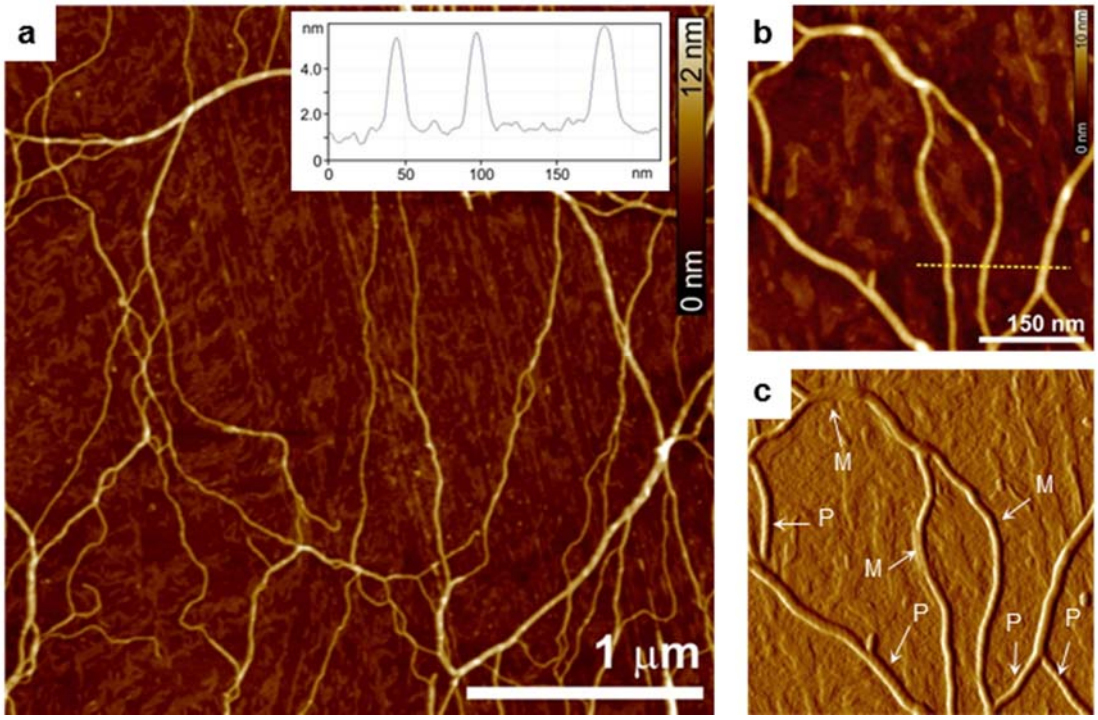



**Figure S5.** (a) AFM height image of fibrous **PBI-1-C4$_{Agg2}$**, spin-coated (3000 rpm) onto silicon substrate from a solution in MCH/toluene (2:1, a*v*/*v*). (b) Zoomed height and (c) phase images of **PBI-1-C4$_{Agg2}$**. Insert: Cross-section analysis corresponding to the yellow dashed line in Figure S5b.

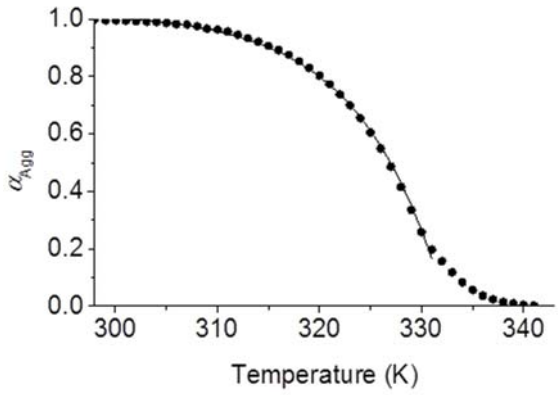



**Figure S6.** Temperature-dependent degree of aggregation ($\alpha_{Agg}$) calculated from the apparent absorption coefficients at $\lambda$ = 523 nm observed upon heating the solution of **PBI-1-C4$_{Agg2}$** at a total concentration of $c_T$ = 5 × $10^{-6}$ M in MCH/toluene (2:1, v/v). The curve shows the resulting fit of the elongation regime calculated according to the cooperative model proposed by Meijer and co-workers.[S2,S3]

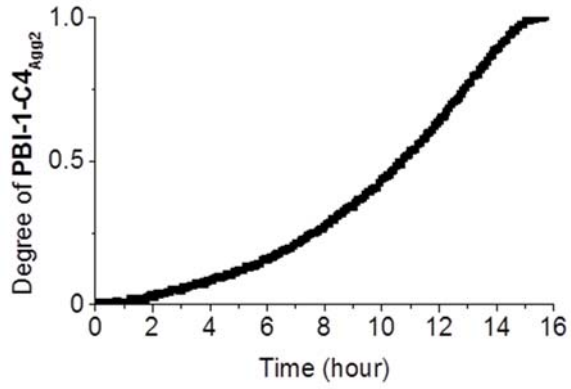



**Figure S7.** Time-dependent degree of **PBI-1-C4$_{Agg2}$** calculated from the apparent absorption coefficients at $\lambda$ = 488 nm observed in the transformation process from **PBI-1-C4$_{Agg1}$** to **PBI-1-C4$_{Agg2}$** in (*S*)-limonene at a concentration of $c_T$ = 2 × $10^{-5}$ M and a temperature of 298 K under stirring at a rate of 400 rpm.

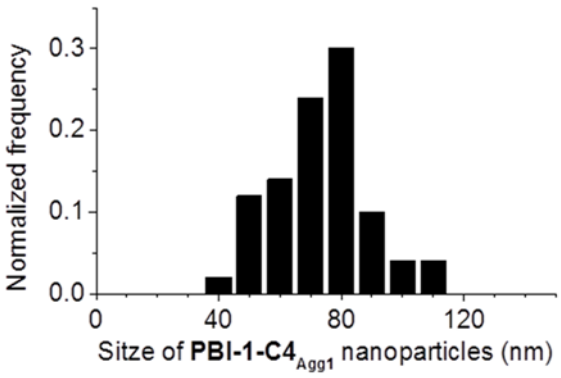



**Figure S8.** Histogram of the size distribution of the nanoparticle-shaped **PBI-1-C4$_{Agg1}$** obtained by tracing 50 objects in the SEM image shown in Figure 8a.

**Table S3.** Morphological parameters of the nanoparticle-shaped **PBI-1-C4$_{Agg1}$** and fibrous **PBI-1-C4$_{Agg2}$** observed in SEM (Figure 8) and AFM images (Figures 4k, 5c, and S5).

| | **SEM sample** (cyclohexane, 1 x $10^{-3}$ M) | **AFM sample** (MCH/toluene (2:1, v/v), 5 x $10^{-6}$ M) |
|---|---|---|
| **PBI-1-C4$_{Agg1}$** (Nanoparticles) | Size: 40-110 nm | Height: 2-8 nm |
| **PBI-1-C4$_{Agg2}$** (Supramolecular polymers) | Length: several micrometers<br>Width: 20-130 nm (agglomeration of fibers) | Length: several micrometers<br>Width: from 4 nm (single fibers) up to 50 nm (agglomeration of fibers) |

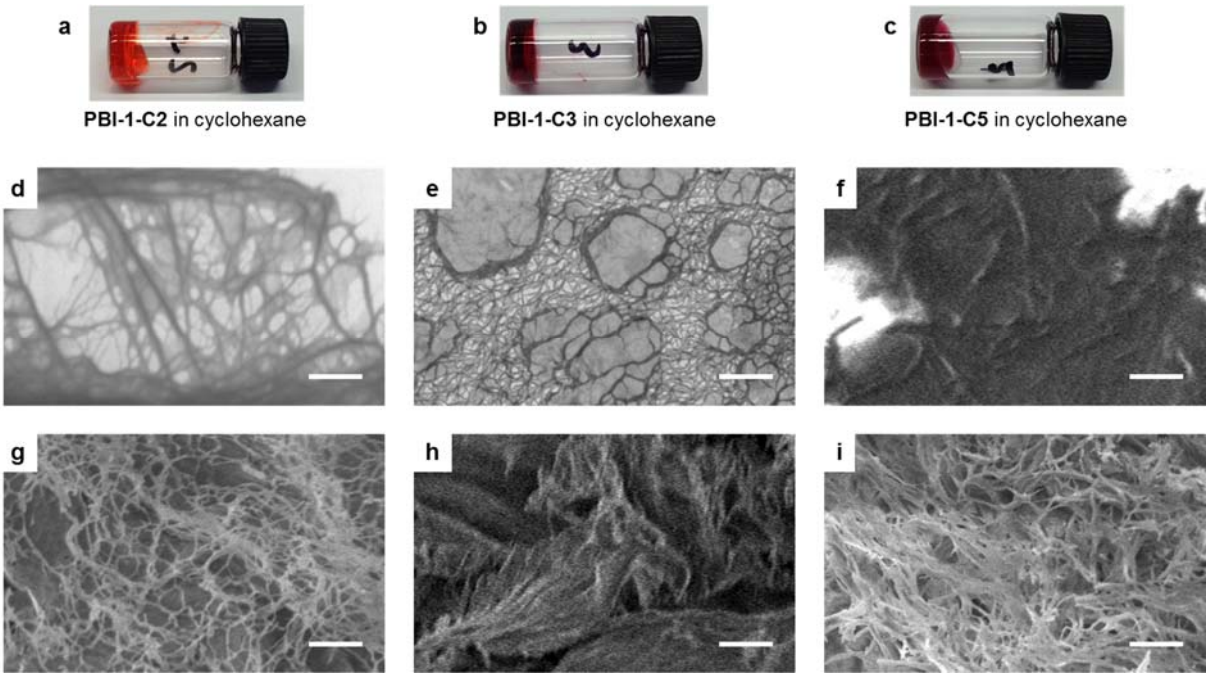



**Figure S9.** (a-c) Photographs of samples of **PBI-1-C2** (a), **PBI-1-C3** (b), and **PBI-1-C5** (c) in cyclohexane ($c_T$ = 1 × $10^{-3}$ M) obtained 1 day after cooling to room temperature. (d-i) SEM images of drop-casted (d-f) and freeze-dried aggregates (g-i) of **PBI-1-C2** (d,g), **PBI-1-C3** (e,h), and **PBI-1-C5** (f,i) on silicon wafers prepared from the samples of each PBIs in cyclohexane. Scale bar, 2 μm.

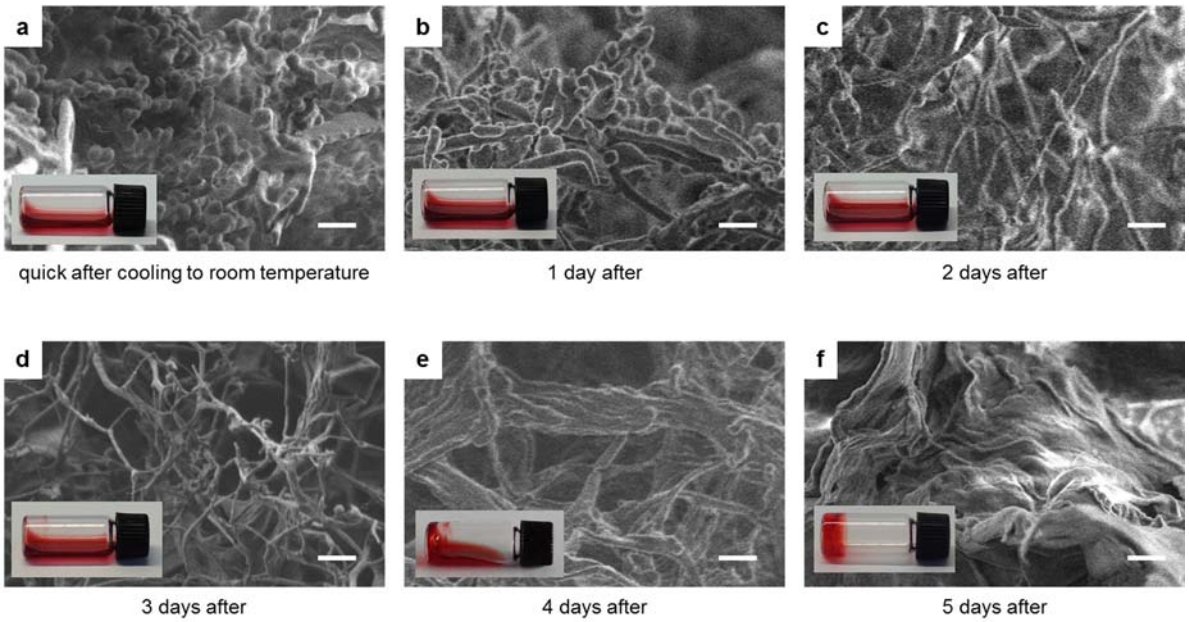



**Figure S10.** (a-f) SEM images of freeze-dried aggregates of **PBI-1-C4** on silicon wafers prepared from the samples of each cyclohexane solutions ($c_T$ = 1 × $10^{-3}$ M) obtained freshly (a), 1 day (b), 2 days (c), 3 days (d), 4 days (e), and 5 days (f) after cooling to room temperature. Scale bar, 2 μm. Inserts: Photographs of solution and gel samples.

## 5. References

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