Electronic Supplementary Information (ESI)

# Thionated PDI Supramolecular Polymers: Controlling Aggregation Mechanisms, Morphology and Function

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## 1. Materials and Equipment

All chemicals were used as purchased and without further purification unless otherwise specified. Solvents used for self-assembly experiments were of HPLC or higher grade where available.

Transmission electron microscopy was carried out using a Gatan Orius SC1000 CCD camera equipped JEOL JEM 1400 microscope operating at 120 kV. Samples were prepared by dropcasting 10  $\mu$ L of solution onto a carbon-coated copper grid, placed on a filter paper to facilitate solvent removal. The ImageJ software package was used to analyse TEM images. Width measurements were obtained by tracing 100+ structures by hand.

Carbon-coated TEM grids were prepared using a Q150TES from Quorum Technologies ltd, to sputter high purity graphite onto mica. Films were floated on deionised water, and deposited onto either 400 or 600 mesh copper grids from Agar Scientific.

UV/Vis spectroscopy measurements were carried out using a Shimadzu UV-2600 spectrometer fitted with ISR-2600 integrating sphere attachment. Samples were placed in a quartz cuvette with 10 mm path length for measurement. Variable temperature UV/Vis measurements were carried out using a Perkin-Elmer Lambda 35 spectrophotometer fitted with Peltier temperature controller. Spectra were recorded at 5 K intervals, allowing a total period of 5 minutes between each measurement for thermal equilibration. Fluorescence spectroscopy measurements were obtained using a PerkinElmer LS-55 spectrometer. In cases where bleed through of the excitation beam was observed, these artefacts were omitted for clarity.

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-ToF) was carried out with a Bruker Ultraflextreme in reflection mode unless samples ionised poorly in which cases linear mode was used. A solution of (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile) in chloroform (at a concentration of 5-10 mg/mL) was used as the matrix for all samples. Matrix and sample solutions (0.1 mg/mL in chloroform) were mixed in a 1:1 (v:v) ratio and approximately 2  $\mu$ l of this mixture was transferred to a polished stainless-steel plate and allowed to dry.

Nuclear magnetic resonance spectra were recorded using a 500 MHz Bruker 500 spectrometer with a cryo-enhanced probe. Sample resonances were referenced to the residual solvent. Due to the small quantities of products available, and exacerbated by the high molecular weights of the products, deviations of some integrals are present. This is particularly apparent with alkyl proton peaks, where trace grease impurities cause a significant increase in the observed integral.

Atomic force microscopy (AFM), Electrostatic force microscopy (EFM) and PeakForce tunnelling AFM (PF-TUNA) were conducted using a Multi-Mode VIII microscope with Nanoscope V controller. Carboncoated mica substrates were prepared through the deposition of <5 nm of high purity graphite onto freshly cleaved mica using a Q150TES from Quorum Technologies Ltd. In each case 10  $\mu$ L of sample solution was dropcast onto the substrate and excess removed either by careful blotting with filter paper, or by applying a slow stream of nitrogen gas. An electrical connection between the sample surface and scanner was created using conductive paint (RS Components Ltd).

AFM experiments were conducted utilising PeakForce feedback in combination with a Fastscan head unit and SCANASYST-AIR-HR cantilevers (nominal tip radius and spring constant 2 nm and 0.4 N/m respectively). This ensures that forces applied to the samples remained in a sub-1nN regime.

EFM experiments were conducted utilising tapping mode feedback to enable qualitative comparison in phase contrast. A grounded cantilever with a conductive PtIr coated tip (nominal tip radius and

spring constant 25 nm and 0.4 N/m respectively) was scanned across the sample in standard tapping mode and then at a lift height of 20 nm. In this way the topography of the sample and its electrostatic interaction with the tip were measured concurrently.

PF-TUNA experiments were conducted utilising PeakForce feedback maintaining a sub-1nN force regime. A conductive PtIr coated tip (nominal tip radius and spring constant 25 nm and 0.4 N/m respectively) was employed with an applied sample bias of 500 mV. In this way the topography of the sample and the contact current passing through it were measured concurrently.

# 2. Synthesis

**Table S1.** Effects of stoichiometry and reaction time on the relative composition of products upon reaction of **PDI1** with Lawesson's Reagent (LR). Percentage composition estimated based on intensity of peaks detected by MALDI-ToF mass spectrometry of crude reaction mixture.

Reaction Conditions		Percentage Composition of Crude Product							
Eq. LR	Time / h	<b>0S</b>	1S	<b>2S</b>	<b>3</b> S	4S	<b>5</b> S	6S	
1	24	47.2	42.3	10.5	0	0	0	0	
2	24	24.9	32.4	33.5	9.1	0	0	0	
8	24	1.19	1.86	19.2	48.7	25.1	2.1	1.9	
8	48	0	1.4	5.0	45.8	44.8	1.7	1.2	
12	48	0	1.3	4.5	46.2	44.8	1.6	1.5	

### Synthesis of PDI1-S1

**PDI1** (7.5 mg, 0.0042 mmol, 1 eq.) was dried into a flask with Lawesson's reagent (1.7 mg, 0.0042 mmol, 1 eq.) and placed under a nitrogen atmosphere. Toluene (anhydrous, 2 mL) was added and the mixture heated to reflux for 24 hours. The mixture was cooled to room temperature, the solvent removed under reduced pressure, and the product purified by preparative TLC (chloroform), followed by a silica gel microcolumn (chloroform). **PDI1-S1** was afforded as a red solid (2.6 mg, 34%).

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.80 (t, J = 4.5 Hz, 1H), 8.64 (d, J = 7.9 Hz, 4H), 8.56 (d, J = 8.1 Hz, 4H), 7.11 (s, 2H), 6.97 (s, 3H), 4.72 – 4.65 (m, 2H), 4.59 – 4.52 (m, 2H), 4.22 (q, J = 4.8 Hz, 2H), 4.06 (t, J = 6.5 Hz, 4H), 4.03 – 3.93 (m, 8H), 3.88 (q, J = 5.2 Hz, 2H), 1.88 – 1.68 (m, 12H), 1.53 – 1.17 (m, 156H), 0.88 – 0.84 (m, 18H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ (ppm) = 198.57, 167.64, 164.45, 164.22, 153.13, 152.85, 141.01, 135.80, 135.19, 134.82, 131.92, 131.79, 129.62, 129.28, 129.19, 128.38, 126.55, 123.55, 123.41, 123.28, 122.95, 105.62, 105.58, 73.65, 73.61, 69.28, 69.24, 47.57, 40.32, 39.92, 37.25, 32.92, 32.10, 32.08, 30.48, 30.19, 29.91, 29.89, 29.86, 29.83, 29.75, 29.64, 29.61, 29.58, 29.55, 29.52, 27.24, 26.36, 26.31, 26.24, 22.86, 22.84, 14.27.

MALDI-ToF MS found 1805.497 m/z, calculated for  $C_{114}H_{172}N_4O_{11}S$ : 1805.27 m/z [M]<sup>-</sup>

### Synthesis of PDI1-S2

**PDI1** (10.0 mg, 0.0056 mmol, 1 eq.) was dried into a flask with Lawesson's reagent (4.5 mg, 0.0112 mmol, 2 eq.) and placed under a nitrogen atmosphere. Toluene (anhydrous, 2 mL) was added and the mixture heated to reflux for 24 hours. The mixture was cooled to room temperature, the solvent removed under reduced pressure, and the product purified by

preparative TLC (chloroform), followed by a silica gel microcolumn (chloroform). **PDI1-S2** was afforded as a red solid (2.2 mg, 22%), alongside comparable amounts of **PDI1-S1**.

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 8.78 (t, *J* = 4.5 Hz, 2H), 8.71 (d, *J* = 8.0 Hz, 4H), 8.64 (d, *J* = 8.1 Hz, 4H), 7.11 (s, 4H), 4.69 (t, *J* = 5.2 Hz, 4H), 4.22 (q, *J* = 4.7 Hz, 4H), 4.07 (t, *J* = 6.5 Hz, 8H), 3.98 (t, *J* = 6.5 Hz, 4H), 1.89 – 1.80 (m, 8H), 1.74 – 1.71 (m, 4H), 1.52 – 1.18 (m, 221H), 0.87–0.84 (m, 20H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ (ppm) = 198.56, 164.52, 152.86, 141.05, 135.76, 135.23, 132.04, 129.71, 126.73, 123.60, 123.12, 105.60, 73.66, 69.23, 47.69, 32.08, 31.75, 30.49, 29.89, 29.85, 29.64, 29.53, 26.36, 26.25, 22.85, 14.27.

MALDI-ToF MS found 1821.343 m/z, calculated for C<sub>114</sub>H<sub>172</sub>N<sub>4</sub>O<sub>10</sub>S<sub>2</sub>: 1821.24 m/z [M]<sup>-</sup>

#### Synthesis of PDI1-S3, cisPDI1-S4, and transPDI1-S4

**PDI1**, (20.0 mg, 0.0112 mmol, 1 eq.) was dried into a flask with Lawesson's reagent (36.1 mg, 0.0894 mmol, 8 eq.) and placed under a nitrogen atmosphere. Toluene (anhydrous, 4 mL) was added and the mixture heated to reflux for 48 hours. The mixture was cooled to room temperature, the solvent removed under reduced pressure, and the obtained products purified in two batches by preparative TLC (chloroform:toluene 7:3 to 9:1), followed by a silica gel microcolumn of each isolated product (chloroform:hexane 1:1 to 9:1). **PDI1-S3** (4.3 mg, 21%), *cis***PDI1-S4** (2.1 mg, 10%), and *trans***PDI1-S4** (1.8 mg, 9%) were afforded as violet (**PDI1-S3**) and deep blue (*cis***PDI1-S4** and *trans***PDI1-S4**) solids.

#### PDI1-S3

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 9.11 (d, *J* = 8.5 Hz, 1H), 8.83 (t, *J* = 4.5 Hz, 1H), 8.77 (t, *J* = 4.5 Hz, 1H), 8.72 – 8.59 (m, 6H), 8.55 (d, *J* = 8.5 Hz, 1H), 7.10 (s, 2H), 7.07 (s, 2H), 5.29 (dd, *J* = 7.5, 3.2 Hz, 2H), 4.69 (dd, *J* = 6.8, 3.4 Hz, 2H), 4.34 (q, *J* = 5.5, 4.9 Hz, 2H), 4.22 (q, *J* = 4.7 Hz, 2H), 4.05 (dt, *J* = 9.9, 6.5 Hz, 9H), 3.97 (td, *J* = 6.6, 4.2 Hz, 4H), 1.87 – 1.80 (m, 8H), 1.76 – 1.68 (m, 4H), 1.52 – 1.19 (m, 123H), 0.87 (m, 20H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ (ppm) = 198.37, 193.71, 152.70, 140.87, 135.63, 135.11, 126.36, 123.61, 122.92, 105.48, 105.48, 73.51, 69.12, 31.95, 31.93, 30.34, 29.75, 29.71, 29.70, 29.61, 29.49, 29.41, 29.38, 26.22, 26.19, 26.10, 22.71, 22.70, 14.12.

**MALDI-ToF MS** found 1837.247 m/z, calculated for  $C_{114}H_{172}N_4O_9S_3$ : 1837.22 m/z [M]<sup>-</sup>

#### transPDI1-S4

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 9.13 (d, J = 8.4 Hz, 2H), 8.83 (t, J = 4.4 Hz, 2H), 8.71 (d, J = 8.0 Hz, 2H), 8.64 (d, J = 8.0 Hz, 2H), 8.61 (d, J = 8.5 Hz, 2H), 7.08 (s, 4H), 5.34 – 5.27 (m, 2H), 4.38 – 4.32 (m, 2H), 4.04 (t, J = 6.5 Hz, 8H), 3.97 (t, J = 6.5 Hz, 4H), 1.87 – 1.70 (m, 12H), 1.51 – 1.20 (m, 95H), 0.90 – 0.83 (m, 18H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ (ppm) = 175.62, 152.84, 134.39, 129.89, 129.64, 105.63, 69.27, 67.93, 39.07, 39.06, 36.06, 32.09, 30.73, 30.51, 29.90, 29.86, 29.75, 29.63, 29.54, 29.48, 29.39, 29.27, 29.14, 27.38, 27.32, 26.34, 26.24, 25.67, 24.14, 23.13, 22.85, 14.27, 14.20, 11.25.

**Partial ROESY** (500 MHz/500 MHz, CDCl<sub>3</sub>)  $\delta^{1}$ H/<sup>1</sup>H (ppm) = 8.71/8.64, 8.64/8.59.

MALDI-ToF MS found 1853.242 m/z, calculated for C<sub>114</sub>H<sub>172</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: 1853.20 m/z [M]<sup>-</sup>

#### cisPDI1-S4

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 9.12 (d, *J* = 8.3 Hz, 2H), 8.82 (d, *J* = 4.9 Hz, 2H), 8.72 (d, *J* = 8.0 Hz, 2H), 8.68 (d, *J* = 8.4 Hz, 2H), 8.58 (d, *J* = 8.7 Hz, 2H), 7.07 (s, 4H), 5.30 (t, *J* = 5.1 Hz, 4H), 4.35 (d, *J* = 5.9 Hz, 4H), 4.04 (t, *J* = 6.5 Hz, 8H), 3.97 (t, *J* = 4.2 Hz, 4H), 1.85 – 1.81 (m, 8H), 1.74 – 1.71 (m, 4H), 1.51 – 1.21 (m, 141H\*), 0.90 – 0.82 (m, 27H\*).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm) = 166.13, 152.85, 134.40, 129.64, 105.63, 73.65, 69.27, 67.93, 39.07, 36.06, 32.10, 32.09, 31.75, 30.73, 30.48, 29.90, 29.86, 29.75, 29.63, 29.56, 29.54, 29.49, 29.40, 29.36, 29.27, 29.15, 27.33, 26.35, 26.24, 25.68, 24.14, 23.13, 22.86, 22.85, 22.81, 14.28, 14.20, 11.25.

**Partial ROESY** (500 MHz/500 MHz, CDCl<sub>3</sub>)  $\delta^{1}$ H/<sup>1</sup>H (ppm) = 8.73/8.68.

MALDI-ToF MS found 1853.173 m/z, calculated for C<sub>114</sub>H<sub>172</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: 1853.20 m/z [M]<sup>-</sup>

# 3. Supplementary Figures



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1( Chemical shift (ppm)

Figure S2. <sup>13</sup>C NMR of **PDI1-S1** in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S4. <sup>13</sup>C NMR of **PDI1-S2** in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S6. <sup>13</sup>C NMR of **PDI1-S3** in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S7. <sup>1</sup>H NMR of *cis*PDI1-S4 in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S8. <sup>13</sup>C NMR of *cis*PDI1-S4 in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S9. <sup>1</sup>H NMR of *trans*PDI1-S4 in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S10. <sup>13</sup>C NMR of *trans*PDI1-S4 in CDCl<sub>3</sub> (asterisk denotes residual solvent peak).



Figure S11. Partial <sup>1</sup>H-<sup>1</sup>H ROESY NMR spectra of *trans*PDI1-S4 (a) and *cis*PDI1-S4 (b) in CDCl<sub>3</sub>.



Figure S12. MALDI-ToF mass spectrum and expansion of **PDI1-S1**.



Figure S13. MALDI-ToF mass spectrum and expansion of PDI1-S2.



Figure S14. MALDI-ToF mass spectrum and expansion of **PDI1-S3**.



Figure S15. MALDI-ToF mass spectrum and expansion of *cis*PDI1-S4.



Figure S16. MALDI-ToF mass spectrum and expansion of *trans*PDI1-S4.



Figure S17. Measured contour widths of *cis*PDI1-S4 nanofibers formed from self-assembly in methylcyclohexane at 5 x  $10^{-5}$  M, determined from TEM images.



Figure S18. Measured contour widths of *trans*PDI1-S4 nanofibers formed from self-assembly in methylcyclohexane at  $5 \times 10^{-5}$  M, determined from TEM images.



Figure S19. Calculated changes in interaction energy for the self-assembly of **PDI1** and its thionated analogues. Values are determined based on reported data from Lee et al. on hydrogen-bonding interactions of thioamides,<sup>1</sup> and Tilley and co-workers for thionated PDI derivatives.<sup>2</sup> All values are given relative to the parent **PDI1** with thionation degree referring to the number of oxygen-to-sulphur substitutions.



Figure S20. Changes in the UV/Vis absorbance spectra of PDI1-S1 (a), PDI1-S2 (b), PDI1-S3 (c), and *cis*PDI1-S4 (b), upon heating from 293 K (red profiles) to 373 K (black profiles) in 5 K intervals. Spectra recorded at a concentration of 5 x 10<sup>-6</sup> M in methylcyclohexane.



Figure S21. Plots of degree of polymerisation (DP<sub>n</sub>) as a function of absolute temperature for
(a) PDI1-S3, (c) *cis*PDI1-S4, and (e) *trans*PDI1-S4. Van't Hoff plots for (b) PDI1-S3, (d)
*cis*PDI1-S4, and (f) *trans*PDI1-S4. All data derived from temperature-dependent UV/Vis spectroscopy measurements.



Figure S22. Peak current values measured during PF-TUNA measurements of representative self-assembled structures of **PDI1**, *cis***PDI1-S4** and *trans***PDI1-S4**. Current values reported are the maximum observed from a current profile extracted orthogonal to the long axis of a fibrous structure for each sample. Profiles were normalised such that the current given is relative to a value of 0 pA for the carbon film background. Error bars represent the background RMSD for each measurement.

### 4. Mechanistic studies

The degree of aggregation at temperature (*T*),  $\alpha$ (*T*), was calculated for each sample using Equation S1, where *Abs*(*T*), *Abs*<sub>agg</sub> and *Abs*<sub>mon</sub> are the absorbance values at a given temperature, and in fully aggregated and fully monomeric states, respectively.

Equation S1.

$$\alpha(T) = \frac{Abs(T) - Abs_{mon}}{Abs_{agg} - Abs_{mon}}$$

For cooperative systems, fitting was attempted according to the nucleation-elongation model proposed by Smulders et al.<sup>3,4</sup> By this method, data in the elongation regime is fitted using Equation S2. The fraction of aggregated molecules is given by an, with an additional factor,  $\alpha_{sat}$ , introduced such that  $\alpha_n/\alpha_{sat}$  is less than 1,  $\Delta H_e$  is the enthalpic change due to binding interactions during elongation, T is the absolute temperature in K,  $T_e$  the elongation temperature, and R the gas constant.

Equation S2. 
$$\alpha_n = \alpha_{sat} \left[ 1 - exp \left( \frac{-\Delta H_e}{RT_e^2} (T - T_e) \right) \right]$$

For the nucleation regime of a cooperative supramolecular polymerisation, fitting is instead carried out according to Equation S3. The additional parameter in this equation,  $K_{\alpha}$ , refers to the dimensionless equilibrium constant.

Equation S3.

$$\alpha_n = K_a^{\frac{1}{3}} exp\left[ \left( \frac{2}{3} K_a^{-\frac{1}{3}} - 1 \right) \frac{\Delta H_e}{RT_e^2} (T - T_e) \right]$$

From the derived parameters the degree of polymerisation of each system may be obtained. The number-averaged degree of polymerisation at the elongation temperature, and therefore the nucleus size, is given by Equation S4.

Equation S4.

At any other given temperature, degree of polymerisation is instead given by Equation S5.

Equation S5. 
$$\langle N_n \rangle = \frac{1}{\sqrt{K_a}} \frac{\alpha_n}{\alpha_{sat} - \alpha_n}$$

 $\langle N_n(T_e)\rangle = \frac{1}{K_a^{\frac{1}{3}}}$ 

For isodesmic systems, data were fit to a sigmoidal Boltzmann function, and the value of  $\alpha$  corrected according to the predicted maximum value from fitting. From the corrected degree of aggregation,  $\alpha$ , the number-averaged degree of polymerisation,  $DP_n$ , was calculated using Equation S6.<sup>5</sup>

Equation S6.

 $DP_n(T) = \frac{1}{\sqrt{1 - \alpha(T)}}$ 

Using the obtained  $DP_n$  value, the equilibrium constant,  $K_e$  is determined using Equation S7, where  $c_T$  is the total concentration.

Equation S7.

 $DP_n(T) = \frac{1}{2} + \frac{1}{2}\sqrt{4K_e(T)c_T + 1}$ 

Based on these parameters, Van't Hoff plots were used to derive the changes in enthalpy and entropy,  $\Delta H$  and  $\Delta S$ , for isodesmic systems, as described by Equation S8.

Equation S8.

Finally, the change in Gibb's free energy,  $\Delta G$ , was determined using Equation S9.

Equation S9.

$$\Delta G = \Delta H - T \Delta S$$

 $lnK_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$ 

**Table S2.** Thermodynamic parameters for **PDI1**, **PDI1-S1**, and **PDI1-S2**, derived from fitting of temperature-dependent changes in UV/Vis spectra and subsequent analysis as described above.

Parameter	Compound					
	PDI1	PDI1-S1	PDI1-S2			
$\Delta H_e$ / kJ mol <sup>-1</sup>	-137.8 ± 2.9	-45.1 ± 1.7	-22.6 ± 0.2			
<i>Те /</i> К	366.2 ± 0.1	352.1 ± 0.7	346.0 ± 0.2			
Ka	8.07E-3 ± 1.32E-2	8.30E-4 ± 7.94E-4	6.08E-5 ± 9.95E-5			
Nn (Te)	4.99	10.64	25.43			
N <sub>n</sub> (293 K)	>10000	385.8	286.3			

**Table S3.** Thermodynamic parameters for **PDI1-S3**, *cis***PDI1-S4**, and *trans***PDI1-S4**, derived from fitting of temperature-dependent changes in UV/Vis spectra and subsequent analysis as described above.

Parameter		Compound				
	PDI1-S3	cisPDI1-S4	transPDI1-S4			
DP <sub>N</sub> (293 K)	3.48	3.18	6.97			
<i>Т<sub>т</sub> /</i> К	322.7	318.9	325.0			
Δ <i>H</i> / kJ mol⁻¹	-78.7	-91.8	-103.5			
ΔS / J mol <sup>-1</sup> K <sup>-1</sup>	-147.5	-192.6	-222.1			
∆G / kJ mol⁻¹	-35.4	-35.4	-38.5			

## 5. References

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