

## Supplementary Information

### A Novel Low-Bandgap Pyridazine Thiadiazole-Based Conjugated Polymer with Deep Molecular Orbital Levels for Organic Photovoltaic Devices

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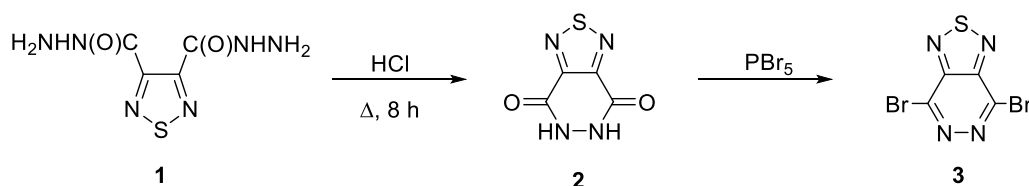
#### 1) General Experimental Information

All reactions were carried out in oven-dried flasks under an inert argon atmosphere and covered with foil unless otherwise indicated and all reactions were stirred magnetically. Anhydrous solvents were used under an inert argon atmosphere. All other chemicals were used as supplied. All reaction mixtures and column eluents were monitored by analytical thin layer chromatography (TLC) using either DC Fertigfolien ALUGRAM aluminium sheets coated with silica gel or Kieselgel 60 F254 Merck, Kenilworth, NJ, USA aluminium sheets. Column chromatography was carried out using Geduran silica gel 60 (40-63 μm). Components were visualised using ultra-violet light (254 nm). Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were taken with either a Bruker AM-300 machine (at 300.1 and 75.5 MHz) with TMS as the standard (Bruker, Billerica, MA, USA) or a 600 MHz Bruker Avance III 600 Cryo spectrometer in the stated solvent using residual protic solvent CHCl<sub>3</sub> (δ = 7.26 ppm, s) as the internal standard. <sup>1</sup>H-NMR chemical shifts are

reported to the nearest 0.01 ppm and quoted using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sxt, sextet; m, multiplet; br, broad; Ar<sub>term</sub>, terminal aromatic or a combination of these. The coupling constants (*J*) are measured in Hertz. <sup>13</sup>C-NMR spectra were recorded at 150 MHz on a spectrometer in the stated solvent using the central reference of CHCl<sub>3</sub> ( $\delta$ = 77.16 ppm, t) as the internal standard. <sup>13</sup>C-NMR chemical shifts are reported to the nearest 0.1 ppm. Mass spectra were obtained using either a Waters LCT, Finnigan MAT 900XP or Waters MALDI micro MX spectrometer at the Department of Chemistry, University College London; or with a MAT INCOS 50 instrument (Thermo Finnigan LLC, San Jose, CA, USA). Some high-resolution MS spectra were measured on a Bruker MICROTOF II instrument using electrospray ionization (ESI, Bruker). The measurement was operated in a positive ion mode (interface capillary voltage 4500 V) or in a negative ion mode (3200 V); mass range was from m/z 50 to 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka Chemicals Ltd., Gillingham, UK). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IR spectra were measured with a Bruker "Alpha-T" instrument (Bruker) in KBr pellets.

## 2) Synthesis of 4,7-Dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine

### 2.1. Synthesis of 4,7-dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine (**3**)



**1,2,5-Thiadiazole-3,4-dicarbohydrazide (1)** was prepared according to the published procedure.<sup>1</sup>

### 5,6-Dihydro[1,2,5]thiadiazolo[3,4-d]pyridazine-4,7-dione (**2**)

A mixture of (**1**) (3.0 g, 14.85 mmol), HCl (conc 4.5 ml) and H<sub>2</sub>O (150 ml) was refluxed for 8 h, cooled to the room temperature. The precipitated product was filtered, washed with H<sub>2</sub>O and dried. Yield 2.2 g (90%). Yellow solid, Mp >300 °C, lit.<sup>2</sup> Mp > 360 °C. IR  $\nu_{\max}$  (KBr, cm<sup>-1</sup>): 3381, 3283, 1670, 1630, 1440, 1389, 1270, 1107, 860, 522. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 12.04 (2H, s). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 150.23, 151.47. HRMS (ESI-TOF), m/z: calcd for C<sub>4</sub>H<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 170.9971, found, 170.9976. MS (EI, 70 eV), m/z (I, %): 170 (M<sup>+</sup>, 64), 140 (6), 84 (23), 58 (34), 29 (100).

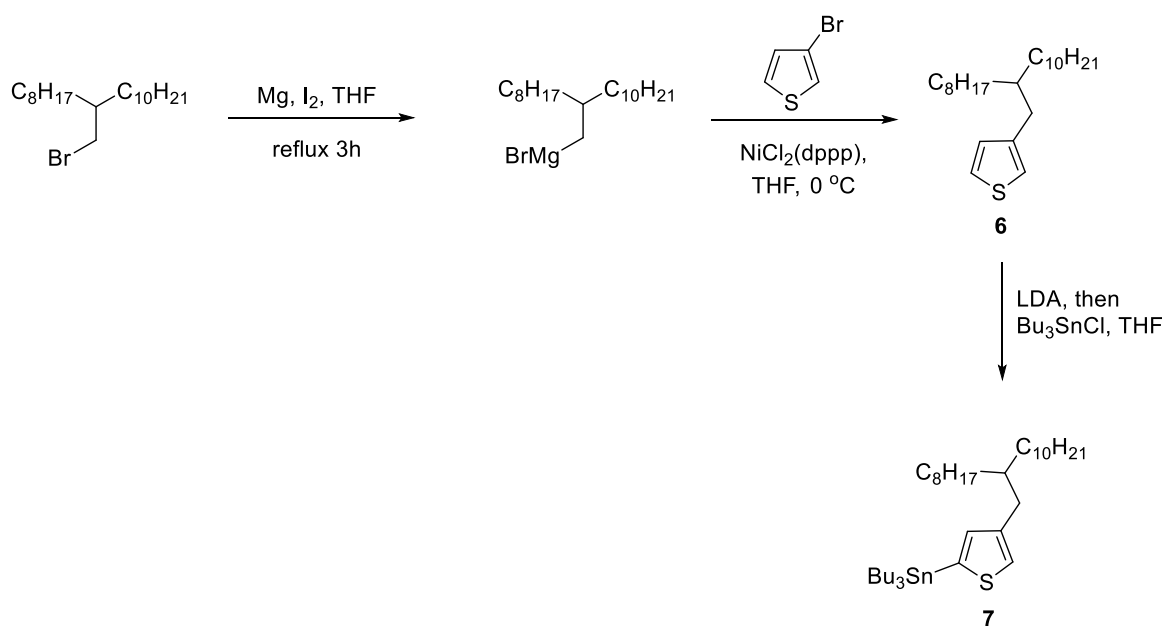
### 4,7-Dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine (**3**)

5,6-Dihydro[1,2,5]thiadiazolo[3,4-d]pyridazine-4,7-dione (**2**) (650 mg, 3.82 mmol) was added to PBr<sub>5</sub> formed by addition of bromine (1.18 ml, 22.92 mmol) to PBr<sub>3</sub> (2.16 ml, 22.92 mmol) at 0 °C. The mixture was stirred for 9 h at 105 °C. The resulting mixture was cooled to the room temperature, poured into ice, washed with CCl<sub>4</sub>, extracted with CHCl<sub>3</sub> (3×40ml) and dried over MgSO<sub>4</sub>. The CHCl<sub>3</sub>

was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel Merck 60, CH<sub>2</sub>Cl<sub>2</sub>) to give the title compound **3**. Yield 845 mg (75%), yellow solid. Mp = 199 – 200 °C. R<sub>f</sub> = 0.5, CH<sub>2</sub>Cl<sub>2</sub>. IR ν<sub>max</sub> (KBr, cm<sup>-1</sup>): 1369, 1361, 1343, 1257, 959, 863, 504. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 142.5, 149.6. HRMS (ESI-TOF), m/z: calcd for C<sub>4</sub><sup>81</sup>Br<sub>2</sub>HN<sub>4</sub>S [M+H]<sup>+</sup>, 296.8262, found, 296.8269. MS, m/z (%): 298 ([M+2]<sup>+</sup>, 22), 296 (M<sup>+</sup>, 49), 294 ([M-2]<sup>+</sup>, 28), 217 (27), 215 (28), 136 (52), 84 (67), 32 (100).

### 3) Synthesis of Pyridine and Pyridazine Thiadiazole Polymers

#### 3.1. Synthesis of tributyl(4-(2-octyldodecyl)thiophen-2-yl)stannane (**7**)



#### 3-(2-Octyldodecyl)thiophene (**6**)

Under an inert atmosphere and to a dry 250 mL round bottomed flask set up for reflux was added magnesium turnings (1.31 g, 54 mmol), iodine (0.34 g, 1.36 mmol), and THF anh. (50 mL). Whilst stirring, a solution of 9-(bromomethyl)nonadecane (15 g) in THF anh. (25 mL) was added dropwise over 25 mins. The resulting mixture was heated to reflux for 3h to afford the brown Grignard reagent. A mixture of 3-bromothiophene (4.3 mL, 45.9 mmol), NiCl<sub>2</sub>(dppp) (0.34 g) and THF anh. (45 mL) was prepared and added to the Grignard reagent dropwise at 0 °C, with vigorous stirring. The resulting mixture was then allowed to warm to RT and stir overnight. The reaction was quenched with 2M hydrochloric acid (HCl:H<sub>2</sub>O, 1:5 v/v). DCM was then added and the organic layer extracted and washed with water three times. The organic layer was dried over MgSO<sub>4</sub> and the solvent evaporated under reduced pressure. The crude product was purified by distillation at 0.21-0.18 mbar at 164-166 °C to afford a yellow oil. Further purification was carried out by passing the oil through silica using hexane as the eluent, affording the pure product as a clear and colourless oil (5.99 g, 40%).

**<sup>1</sup>H NMR** (600 MHz CDCl<sub>3</sub>) δ (ppm): 7.23 (dd, *J* = 4.9, 2.9 Hz, 1H, ThH), 6.90 (m, 2H, ThH), 2.56 (d, *J* = 6.8 Hz, 2H, ThCH<sub>2</sub>), 1.60 (m, 1H, CH<sub>2</sub>CH), 1.34-1.19 (m, 32H, CH<sub>2</sub>), 0.89 (t, *J* = 7.0 Hz, 6H, CH<sub>3</sub>). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): 142.1, 128.9, 124.9, 120.8, 39.0, 34.8, 33.4, 32.0, 30.1, 29.8, 29.8, 29.5, 29.5, 26.7, 22.8, 14.3.

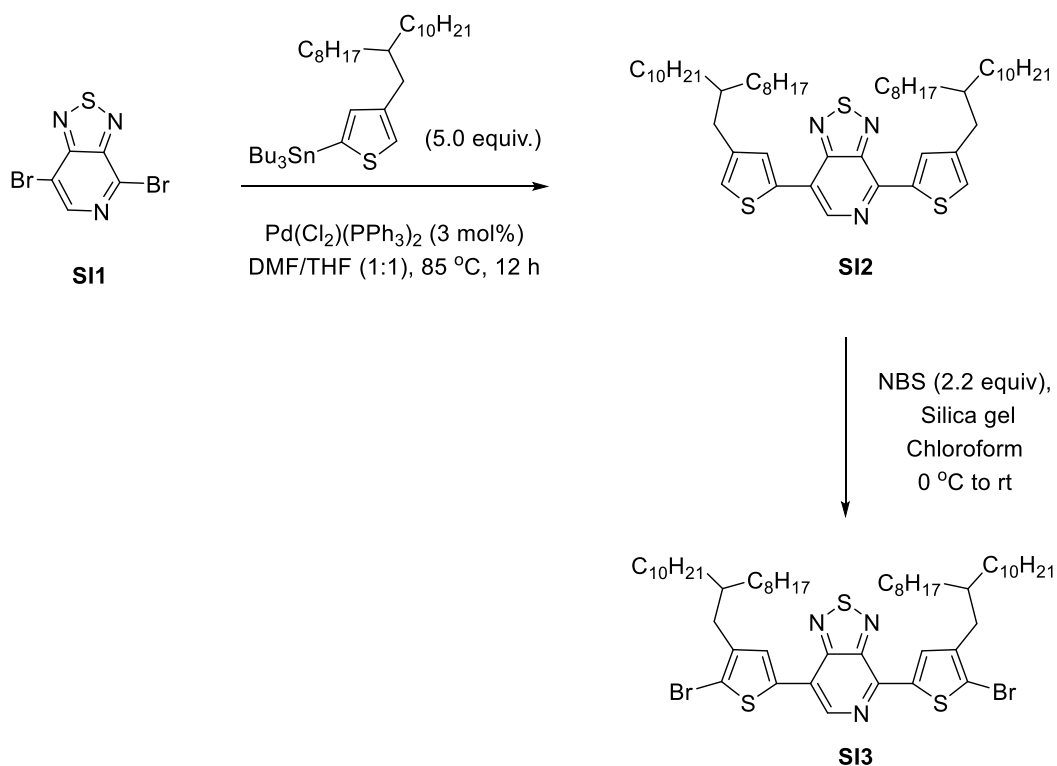
Spectroscopic data is supported by the literature.<sup>2</sup>

### Tributyl(4-(2-octyldodecyl)thiophen-2-yl)stannane (7)

To a 250 mL three-necked round bottomed flask was added 3-(2-octyldodecyl)thiophene (**6**) (5.3 g, 14.5 mmol) and THF anh. (50 mL). The clear and colourless solution was cooled to -78 °C and degassed. A solution of lithium diisopropylamide (2M, 9 mL, 18 mmol) was then added dropwise to the flask. The mixture was stirred at -78 °C for 1h and then at 0 °C for an additional 1h. The reaction was cooled to -78 °C again before tributylstannylchloride (5.8 mL, 21.4 mmol) was added all at once. The mixture was then allowed to warm to RT and stir overnight. The resulting mixture was washed with water and extracted with ether. The organic layer was dried over MgSO<sub>4</sub> and then concentrated in *vacuo* to afford clear and yellow oil, which was further dried under high vacuum. The title product was used in subsequent reactions without further purification (12.58 g).

**Crude <sup>1</sup>H NMR** (600 MHz CDCl<sub>3</sub>) δ (ppm): 7.15 (s, 1H, ThH), 6.92 (s, 1H, ThH), 2.59 (d, *J* = 6.8 Hz, 2H, ThCH<sub>2</sub>), 1.60 (m, 1H, CH<sub>2</sub>CH), 1.40-1.04 (m, 32H, CH<sub>2</sub>), 0.96-0.84 (m, 6H, CH<sub>3</sub>). **<sup>13</sup>C NMR**: Not acquired as compound was not purified.

### 3.2. Synthesis of Dibrominated Monomer (SI3)



**4,7-Dibromo[1,2,5]thiadiazolo[3,4-c]pyridine (SI1)** was prepared according to the published procedure.<sup>3</sup>

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#### **4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (SI2)**

To a 10 mL microwave vial equipped with a magnetic stirrer bar was added (**SI1**) (0.15 g, 0.51 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.1 mg, 0.016 mmol, 3 mol%) and tributyl(4-(2-octyldodecyl)thiophen-2-yl)stannane (**7**) (1.60 g, 2.45 mmol, 5 equiv.) in anhydrous DMF (2.7 mL) and THF (2.7 mL). The resulting mixture was stirred and degassed for 1 h before being heated to 85 °C and left to stir overnight. The resulting bright red mixture was washed with water and the organic layer extracted with ether, dried over MgSO<sub>4</sub> and then concentrated *in vacuo*. The crude compound was passed through silica eluting with hexane:chloroform (9:1) to afford the purified product as a red oily residue (0.094 g, 21%).

<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) δ (ppm): 8.81 (s, 1H, PhHN), 8.50 (d, *J* = 1.2 Hz, 1H, ThH), 7.93 (d, *J* = 1.2 Hz, 1H, ThH), 7.17 (s, 1H, ThH), 7.04 (s, 1H, ThH), 2.64 (dd, *J* = 8.8, 7.1 Hz, 4H, ThCH<sub>2</sub>CH), 1.74-1.69 (m, 2H, CH<sub>2</sub>CH), 1.40-1.14 (m, 64H, CH<sub>2</sub>), 0.91-0.84 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): 155.0, 148.2, 146.5, 144.1, 143.3, 141.2, 141.0, 136.1, 133.8, 130.0, 126.7, 123.0, 120.6, 39.0, 40.0, 35.2, 35.1, 33.4, 32.1, 31.7, 30.2, 29.8, 29.8, 29.5, 26.8, 22.8, 14.3. LRMS: (CI+): *m/z* 860 [M-2H]<sup>+</sup>.

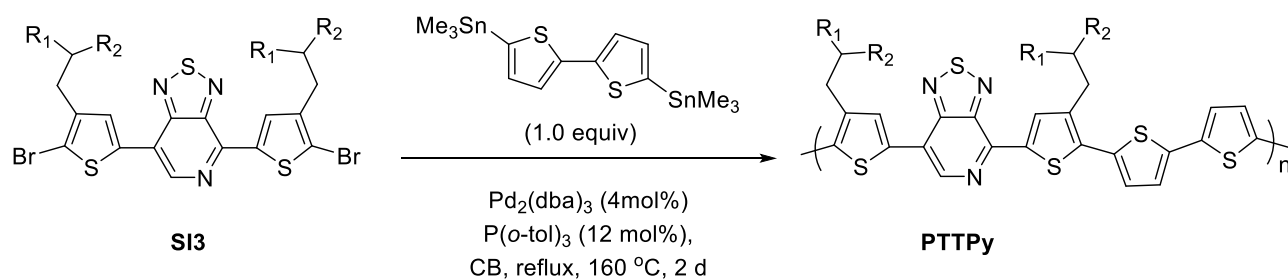
#### **4,7-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (SI3)**

To a solution of (**SI2**) (0.092 g, 0.11 mmol) in 4 mL of chloroform was added silica gel (4 mg). The mixture was cooled to 0 °C before NBS (0.042 g, 0.24 mmol, 2.2 equiv.) was added all at once. The mixture was allowed to stir at 0 °C for 30 mins and then at RT overnight. The resulting deep red mixture was concentrated *in vacuo*. The crude red compound was passed through silica, eluting with hexane:chloroform (9:1) to afford the title compound as a red oily residue.

Monobrominated product and unreacted SM was recovered using the same eluent (*R<sub>F</sub>*=0.68) and was recycled using the same procedure by adding 1.5 equiv. of NBS to form more of the dibrominated product. Combined with previously isolated dibrominated monomer, the title compound was isolated as a red oily residue (0.095 g, 89%).

<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) δ (ppm): 8.70 (s, 1H, PhHN), 8.33 (s, 1H, ThH), 7.75 (s, 1H, ThH), 2.59 (dd, *J* = 9.3, 7.3 Hz, 4H, ThCH<sub>2</sub>CH), 1.75 (m, 2H, CH<sub>2</sub>CH), 1.28 (m, 64H, CH<sub>2</sub>), 0.90-0.84 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): 154.7, 147.9, 145.6, 143.6, 142.7, 140.9, 140.3, 135.8, 133.3, 129.2, 120.0, 117.2, 112.7, 38.6, 38.6, 34.5, 34.3, 33.5, 32.0, 31.7, 31.1, 30.1, 29.8, 29.8, 29.8, 29.5, 26.7, 22.8, 22.8, 14.3. LRMS: (MALDI): *m/z*: 1017, 1019, 1021 [M]<sup>+</sup>.

### 3.3. Synthesis of **PTTPy**



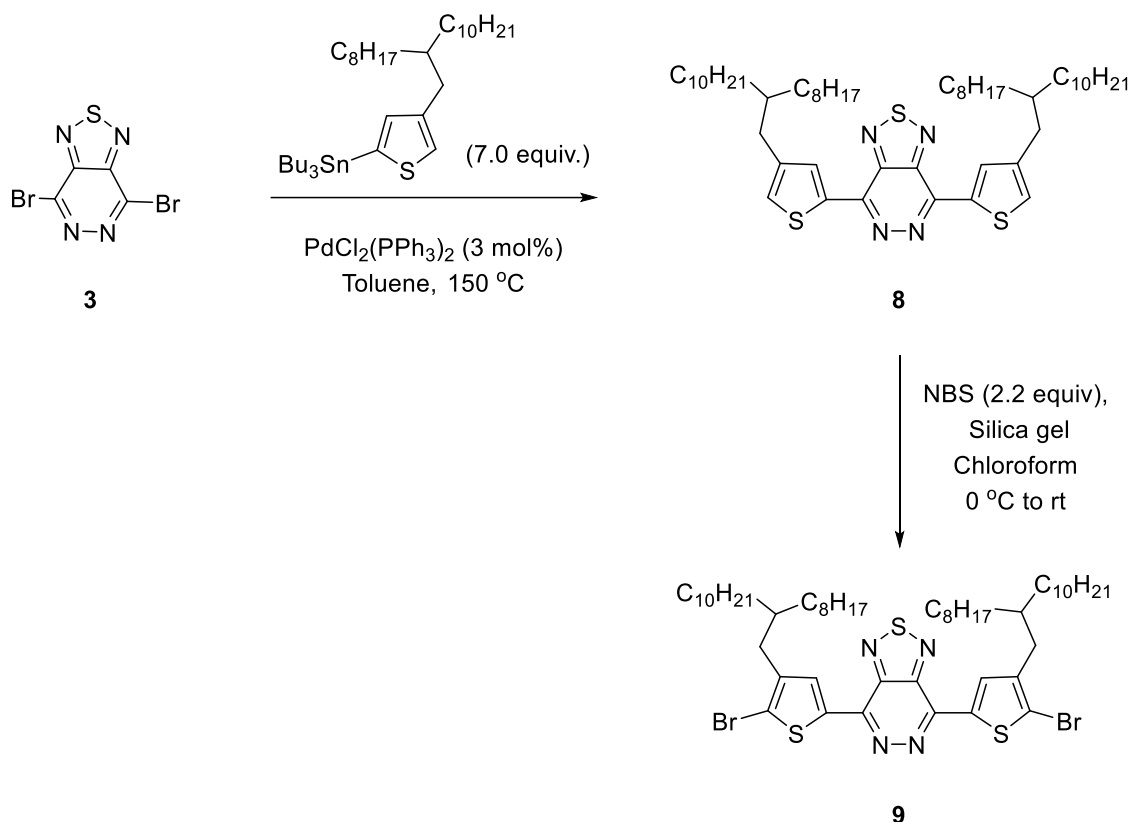
R<sub>1</sub>: C<sub>10</sub>H<sub>21</sub>  
R<sub>2</sub>: C<sub>8</sub>H<sub>17</sub>

#### **PTTPy**

To a 2 mL microwave vial equipped with a magnetic stirrer was added (**SI3**) (0.060 g, 0.059 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.029 g, 0.059 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.0023 g, 0.0025 mmol, 4 mol %) and tri(*o*-tolylphosphine) (0.0031 g, 0.010 mmol, 16 mol%). The vial was then sealed shut before anhydrous chlorobenzene (1 mL) was added. The mixture was degassed for 30 mins and then heated to 160 °C for 2d. The resulting mixture (indigo/green) in colour was diluted with chlorobenzene (5 mL) and then slowly precipitated into methanol (25 mL). The solid was filtered into an extraction thimble and then subjected to Soxhlet extraction with acetone, hexane and finally chloroform. The chloroform fraction was concentrated *in vacuo* and re-dissolved in 3 mL of chlorobenzene. The solution was then precipitated into cold methanol (10 mL), filtered and then dried under vacuum to obtain a dark green solid (0.017 g, 28%).

GPC was performed to isolate higher molecular weight fractions (>10 kDa). These were combined, concentrated *in vacuo*, diluted in 3 mL of chlorobenzene, precipitated into methanol (10 mL), and filtered to afford the polymer as a dark green solid (0.0018 g, 3%). Absorption maximum (chlorobenzene):  $\lambda_{\text{max}}$  673 (thin film),  $\lambda_{\text{max}}$  621 (solution); GPC (polystyrene standard):  $M_n$  = 41 kDa,  $M_w$  = 49 kDa, PDI = 1.2.

### 3.4. Synthesis of Dibrominated Monomer (**9**)



#### 4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-d]pyridazine (**8**)

To a 10 mL microwave vial equipped with a magnetic stirrer bar was added (**3**) (0.078 g, 0.27 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (5.7 mg, 0.0081 mmol) and tributyl(4-(2-octyldodecyl)thiophen-2-yl)stannane (**2**) (1.22 g, 1.86 mmol, 7 equiv.), followed by anhydrous toluene (1.7 mL). The resulting cloudy yellow mixture was degassed for 1 h and then heated to 150 °C overnight. The resulting brown/ red mixture was washed with water and the organic layer extracted with ether, dried over  $\text{MgSO}_4$  and then concentrated *in vacuo*. The crude compound was passed through silica eluting with hexane:chloroform (5:1) to afford the purified product as a red oily residue (0.05 g, 22%).

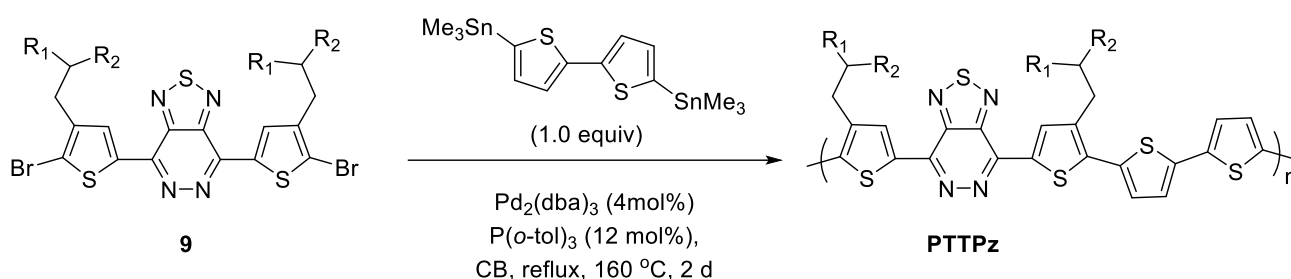
$^1\text{H NMR}$  (600 MHz  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.47 (d,  $J = 1.2$  Hz, 2H, ThH), 7.20 (d,  $J = 1.2$  Hz, 2H, ThH), 2.64 (d,  $J = 6.8$  Hz, 4H, Th $\text{CH}_2\text{CH}$ ), 1.73-1.68 (m, 2H,  $\text{CH}_2\text{CH}$ ), 1.40-1.13 (m, 64H,  $\text{CH}_2$ ), 0.87 (t,  $J = 6.9$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ): 148.3, 148.0, 143.9, 137.6, 134.5, 127.6, 39.1, 35.1, 33.4, 32.1, 30.2, 29.8, 29.8, 29.5, 26.8, 22.8, 14.3. **LRMS**: (MALDI):  $m/z$  863  $[\text{M}]^+$ .

### 4,7-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-d]pyridazine (**9**)

To a solution of (**8**) (0.057 g, 0.065 mmol) in 4 mL of chloroform was added silica gel (2.4 mg). The mixture was cooled to 0 °C before NBS (0.026 g, 0.14 mmol, 2.2 equiv.) was added all at once. The mixture was allowed to stir at 0 °C for 30 mins and then at RT overnight. The resulting deep red mixture was concentrated *in vacuo*. Reaction did not complete, therefore an extra 0.5 equiv. of NBS (0.058 g) was added and the reaction was monitored by TLC, adding more NBS when necessary (0.5 equiv. at a time). After a total of 2.0 equiv. of NBS added, reaction was concentrated *in vacuo*. The crude compound was passed through silica, eluting with hexane:chloroform (2:1). The title compound was isolated as a red oily residue (0.067 g, 100%).

<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) δ (ppm): 8.33 (s, 2H, ThH), 2.60 (d, *J* = 7.2 Hz, 4H, ThCH<sub>2</sub>CH), 1.77 (m, 2H, CH<sub>2</sub>CH), 1.40-1.17 (m, 64H, CH<sub>2</sub>), 0.91-0.83 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): 147.8, 147.6, 143.5, 137.3, 134.2, 118.2, 38.6, 34.4, 33.5, 32.0, 31.1, 30.1, 29.8, 29.8, 29.8, 29.5, 26.7, 22.8, 14.3. LRMS: (MALDI): *m/z*: 1018, 1020, 1022 [M]<sup>+</sup>.

### 3.5. Synthesis of PTPPz



R<sub>1</sub>: C<sub>10</sub>H<sub>21</sub>  
R<sub>2</sub>: C<sub>8</sub>H<sub>17</sub>

### PTPPz

To a 2 mL microwave vial equipped with a magnetic stirrer was added (**9**) (0.045 g, 0.044 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.022 g, 0.044 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.0018 g, 0.0020 mmol, 4 mol %) and tri(*o*-tolylphosphine) (0.0025 g, 0.0082 mmol, 16 mol%). The vial was then sealed shut before anhydrous chlorobenzene (1 mL) was added. The mixture was degassed for 30 mins and then heated to 160 °C for 2d. The resulting mixture (indigo/green) in colour was diluted with chlorobenzene (5 mL) and then slowly precipitated into methanol (25 mL). The solid was filtered into an extraction thimble and then subjected to Soxhlet extraction with acetone and hexane. The hexane fraction was concentrated *in vacuo* and re-dissolved in 3 mL of chlorobenzene. The solution was then precipitated into cold methanol (10 mL), filtered and then dried under vacuum to obtain a dark green solid (0.040 g, 88%).

GPC was performed to isolate higher molecular weight fractions (>10 kDa). These were combined, concentrated *in vacuo*, diluted in 3 mL of chlorobenzene, precipitated into methanol (10 mL), and filtered to afford the polymer as a dark green solid (0.0011 g, 24%). Absorption maximum

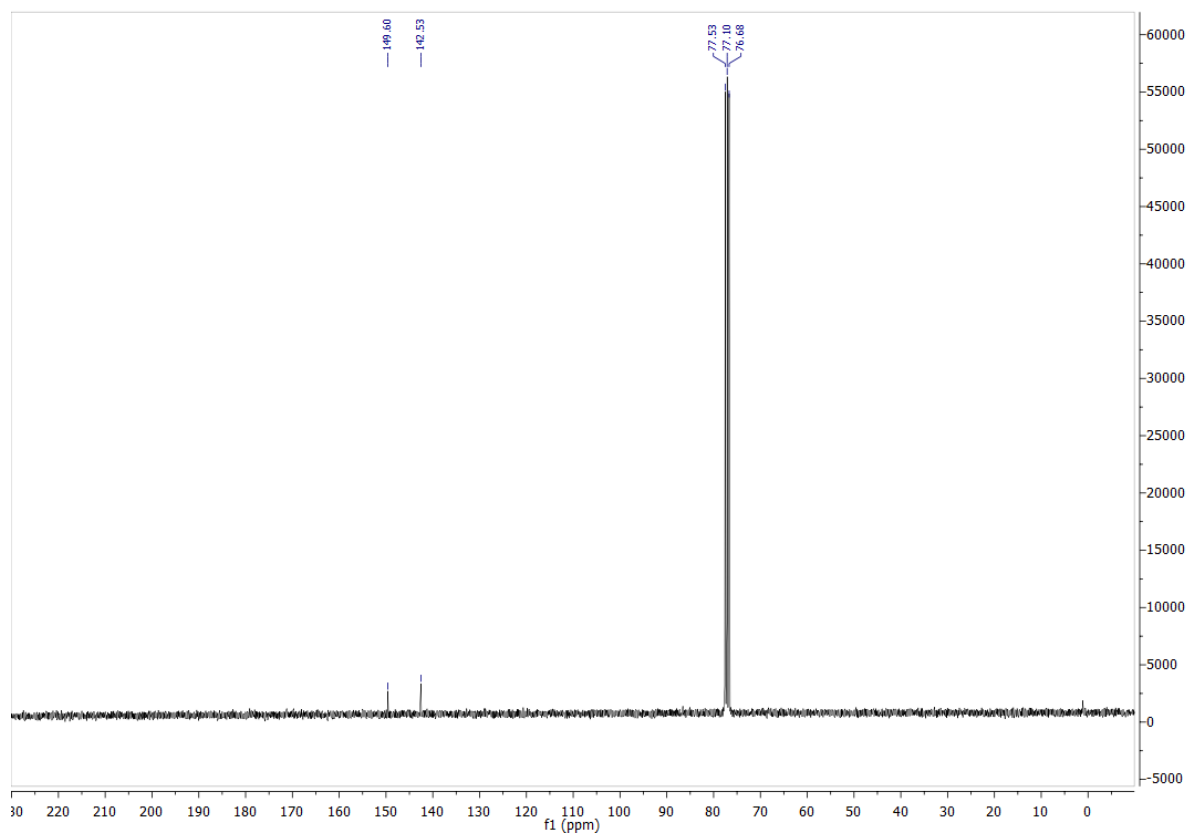
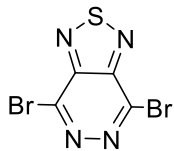


(chlorobenzene):  $\lambda_{\max}$  692 (thin film),  $\lambda_{\max}$  627 (solution); GPC (polystyrene standard):  $M_n$  = 20 kDa,  $M_w$  = 26 kDa, PDI = 1.3.

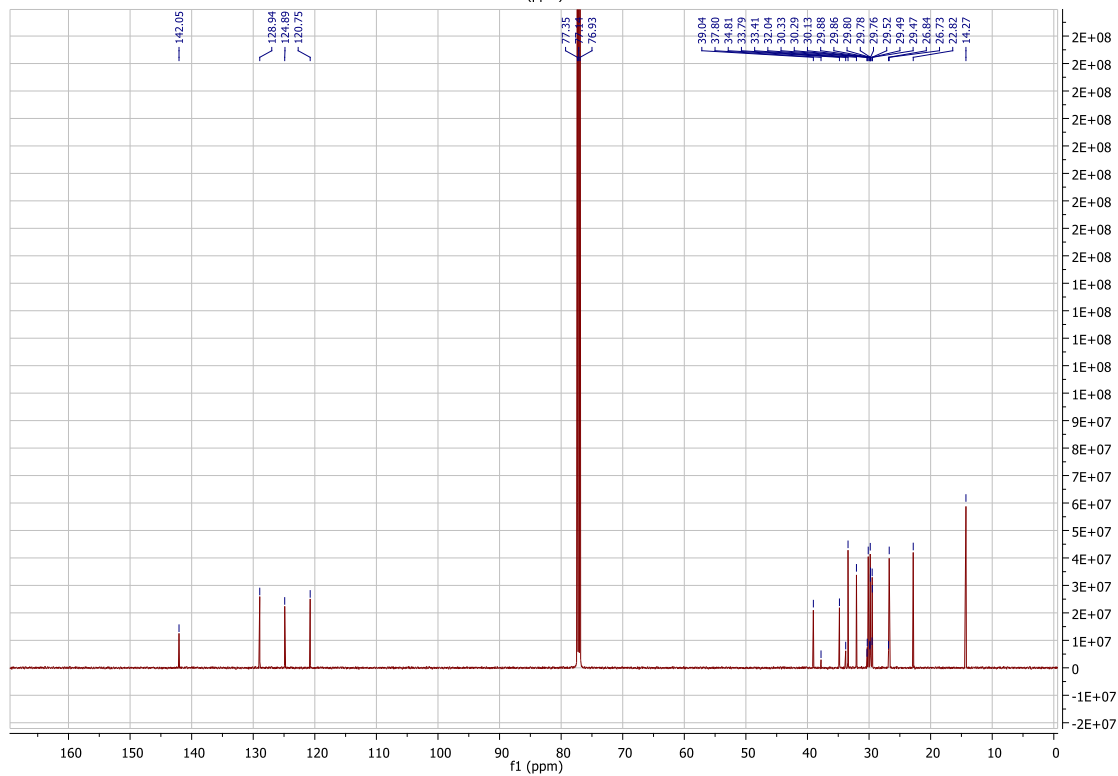
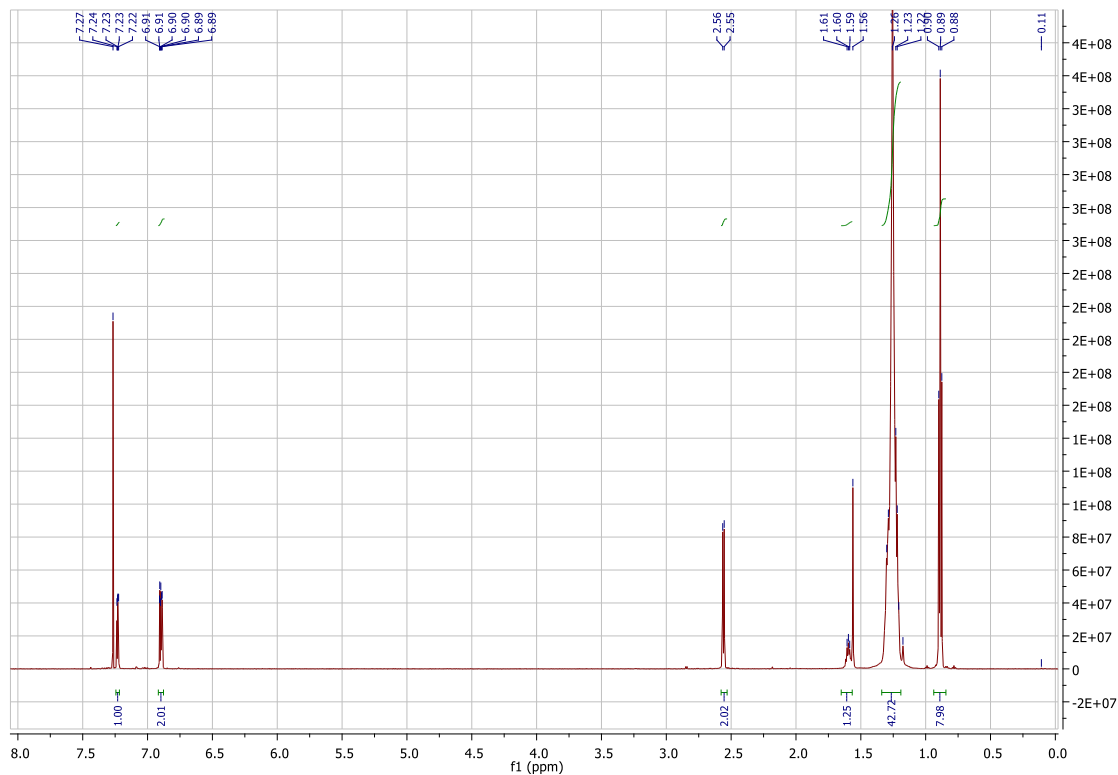
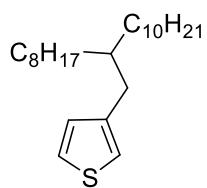
**Variable Temperature  $^1\text{H}$  NMR** (500 MHz  $\text{CDCl}_3$ ) was obtained after 512 scans at 50 °C, however peaks were unable to be individually identified/ resolved due to broadening caused by aggregation.

#### 4) $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR Spectra

##### 4,7-Dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine (3)

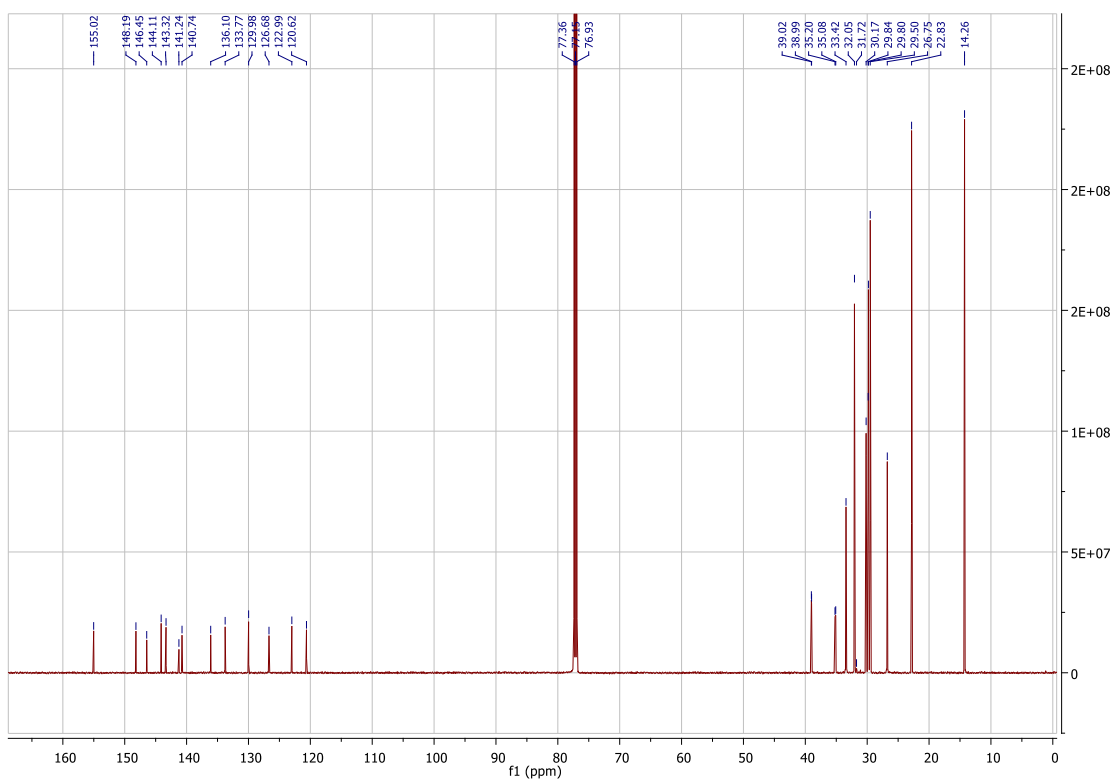
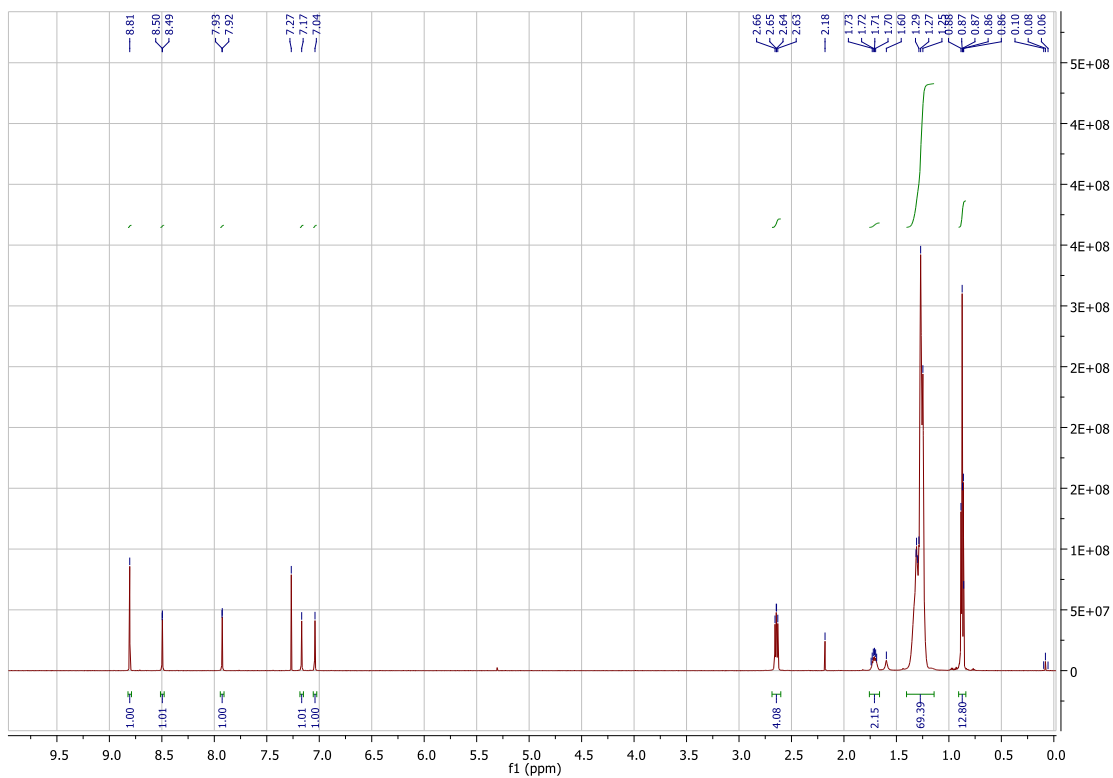
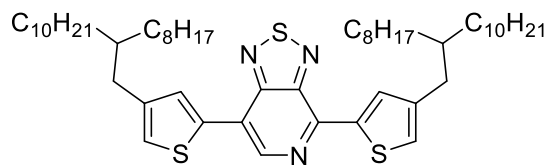


### 3-(2-Octyldodecyl)thiophene (6)



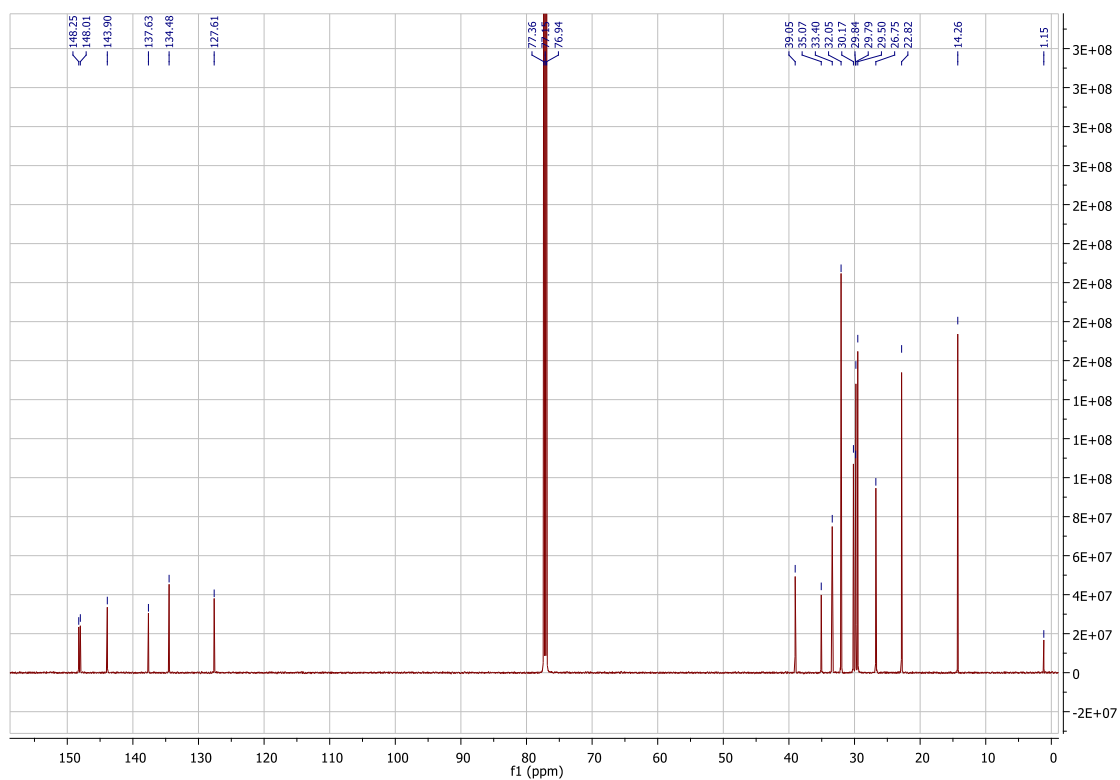
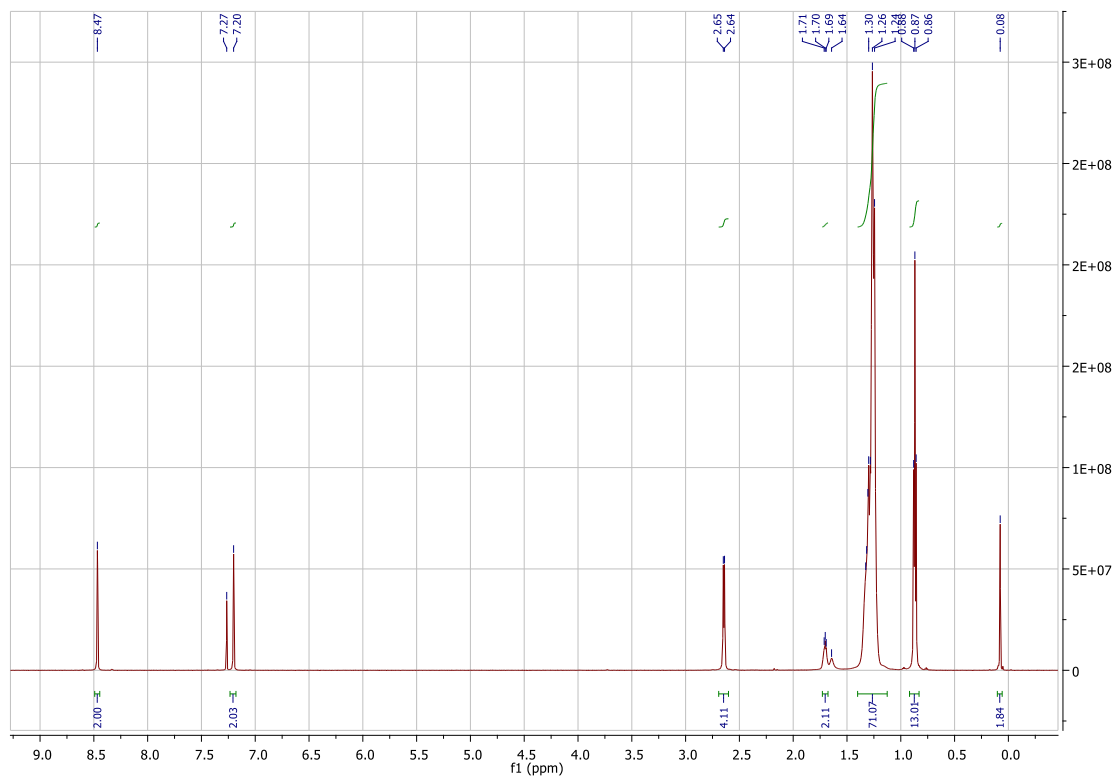
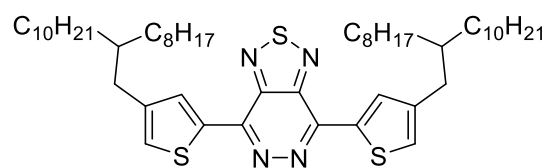


4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (S12)

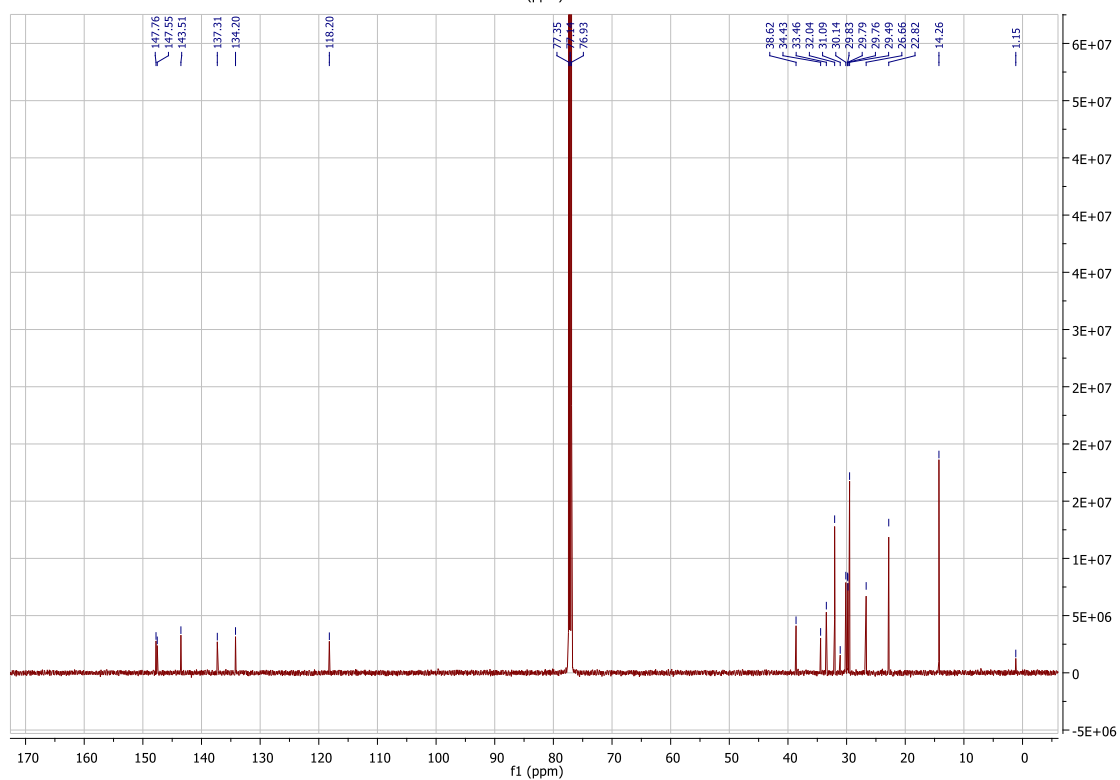
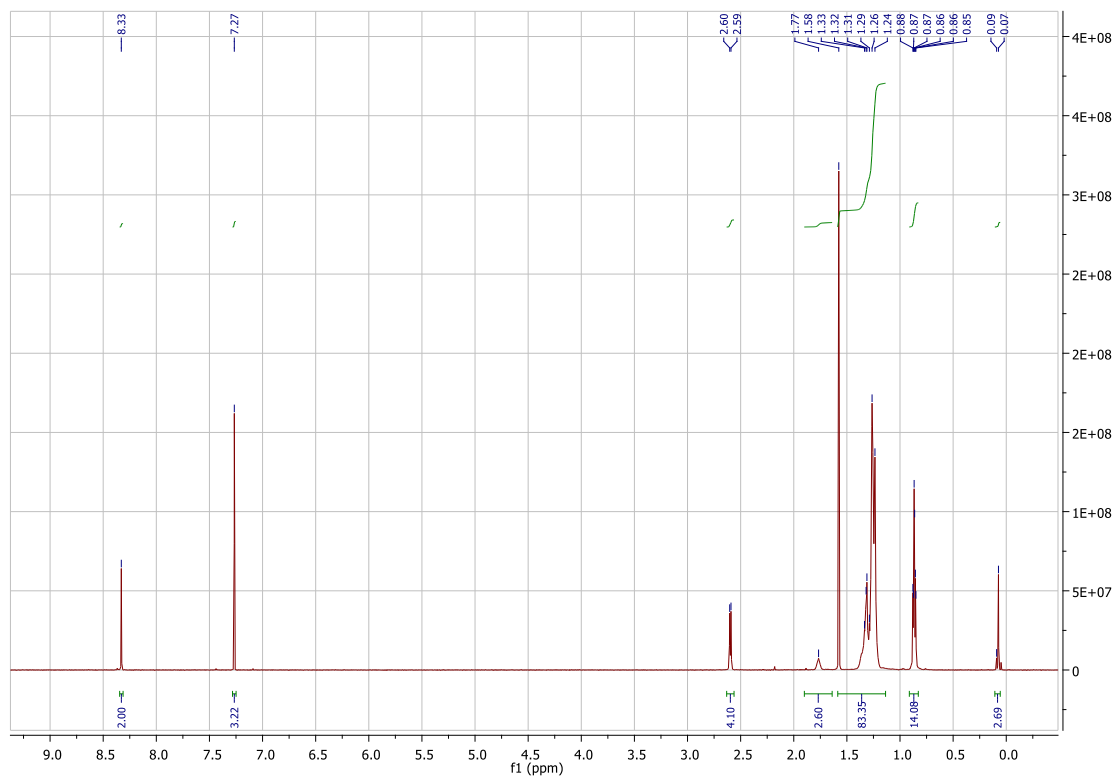
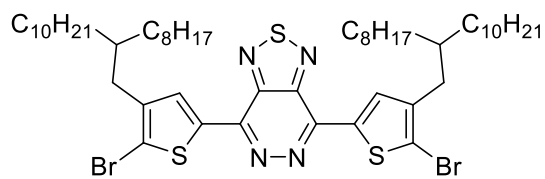




### 4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-d]pyridazine (8)

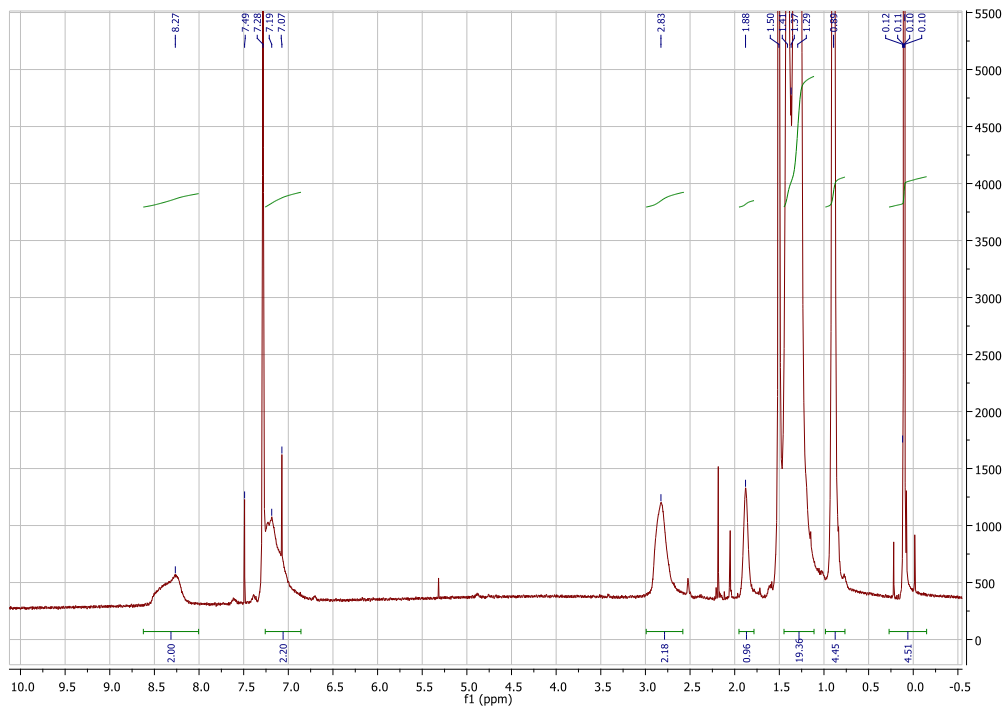
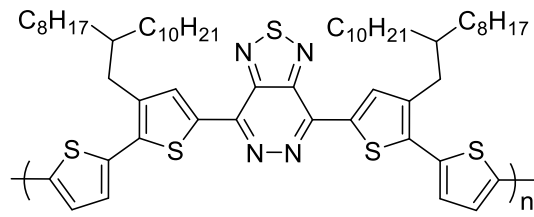


**4,7-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-d]pyridazine (9)**





# PTTPz



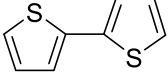
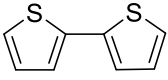
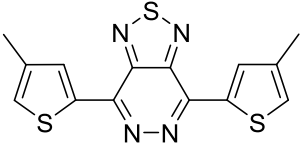
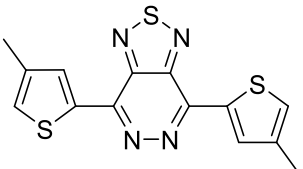
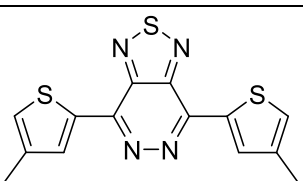
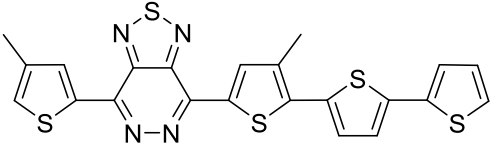
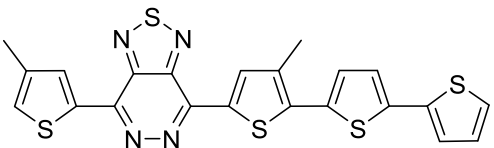
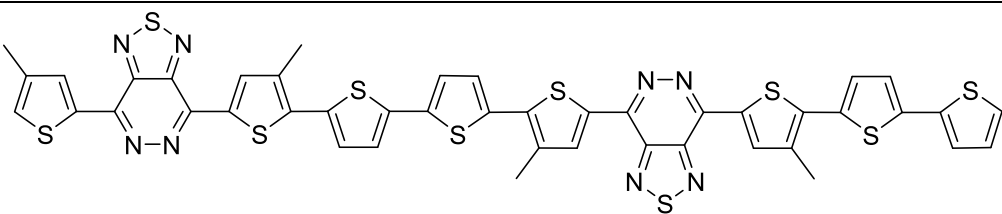
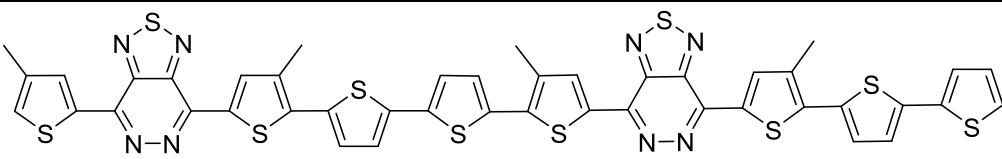
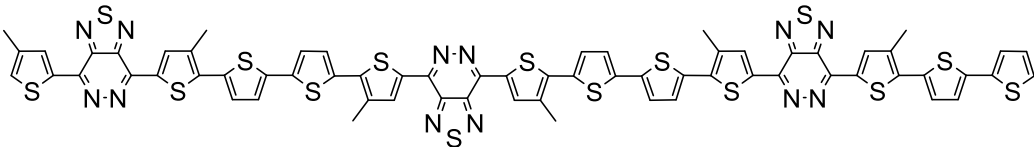
## 5) DFT Calculations

### 5.1. Method

The ground state geometries (DFT-D3) were obtained by B3LYP density functional method with basis set def2-SVP. The dispersion correction was conducted by Grimme's D3 version with the BJ damping function.<sup>4</sup>

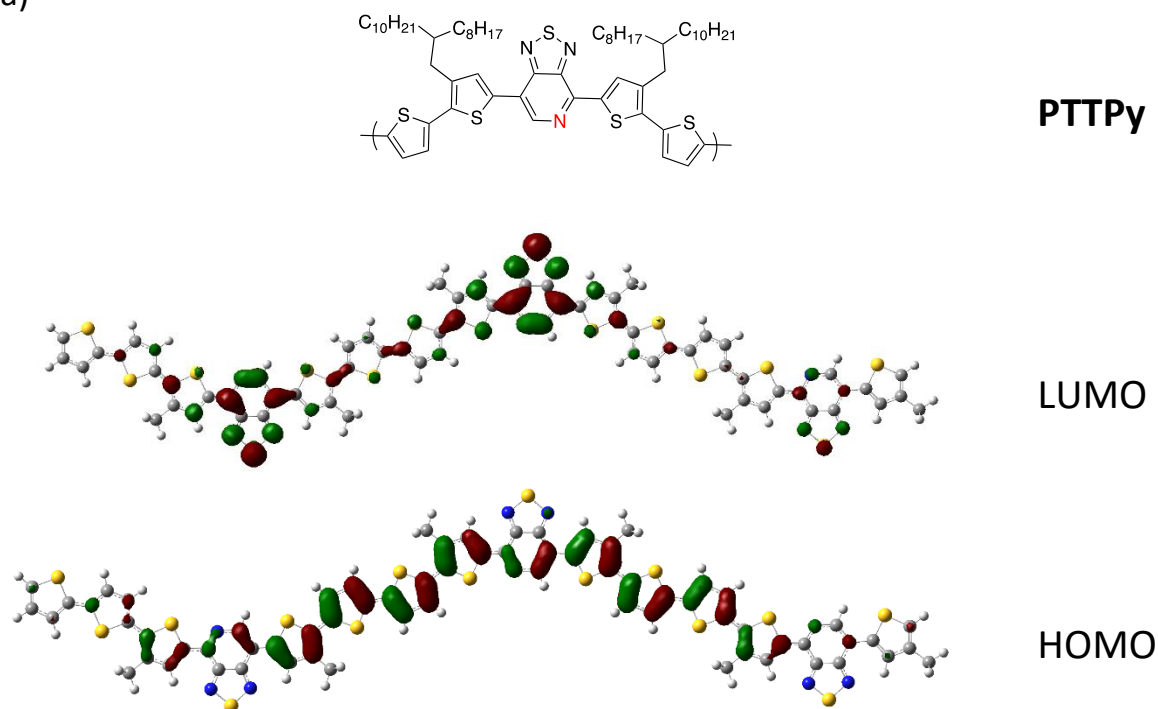
### 5.2. Geometry-Optimised Structures

*Table S1: Geometry-optimised ground-state structures of pyridazine thiadiazole intermediates and their corresponding energies  $E(\text{RB3LYP})$ . The lowest energy conformers of each type of intermediate (i.e. pyridazine thiadiazole (PzT), co-monomer (bithiophene), monomer, dimer and trimer) are indicated in bold. Octyl-dodecyl chains were substituted for methyl groups for simplicity.*

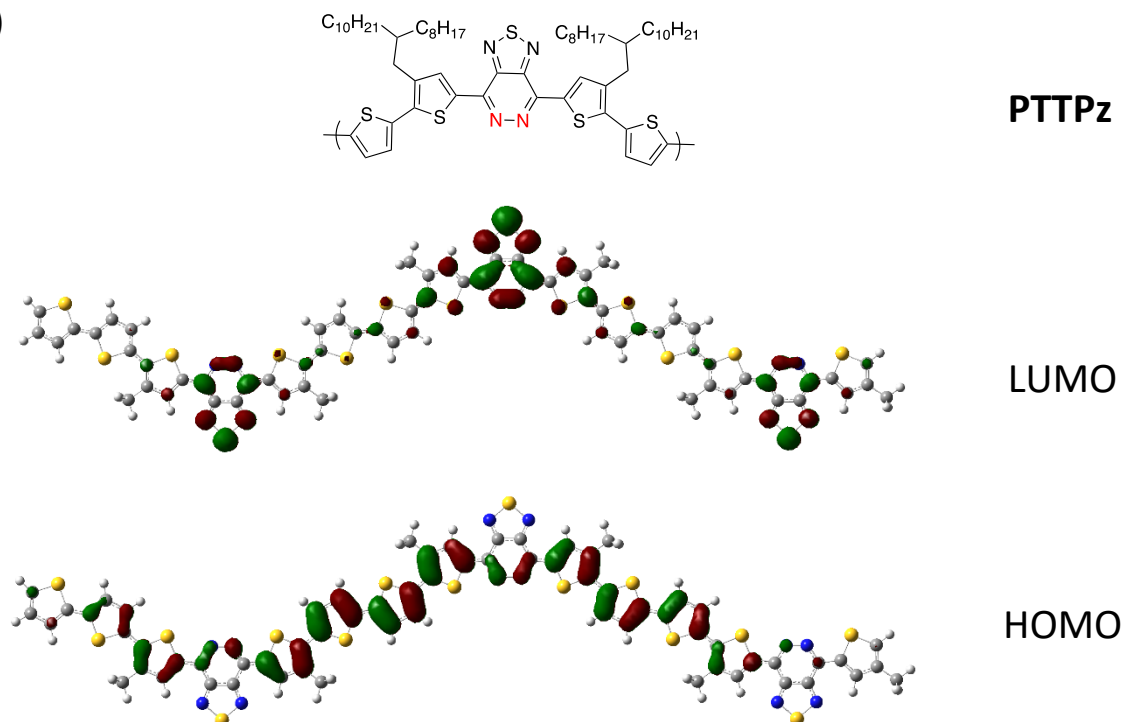
	Geometry-Optimised Ground-State Structures	E(RB3LYP) (a.u.)
Bithiophene_1		-1104.42224740
Bithiophene_2		-1104.42089486
PzT_1		-1952.23009546
PzT_2		-1952.22816002
PzT_3		-1952.22613286
Monomer_1		-3055.47548266
Monomer_2		-3055.47420806
Dimer_1		-6109.77456031
Dimer_2		-6109.77304577
Trimer		-9164.07362696

Scheme S1: Geometry-optimised structures and molecular orbital distributions of a) **PTTPy** and b) **PTTPz** using DFT-D3 at the level of B3LYP/def2-SVP.

a)



b)



### 5.3. Theoretical Optical Properties

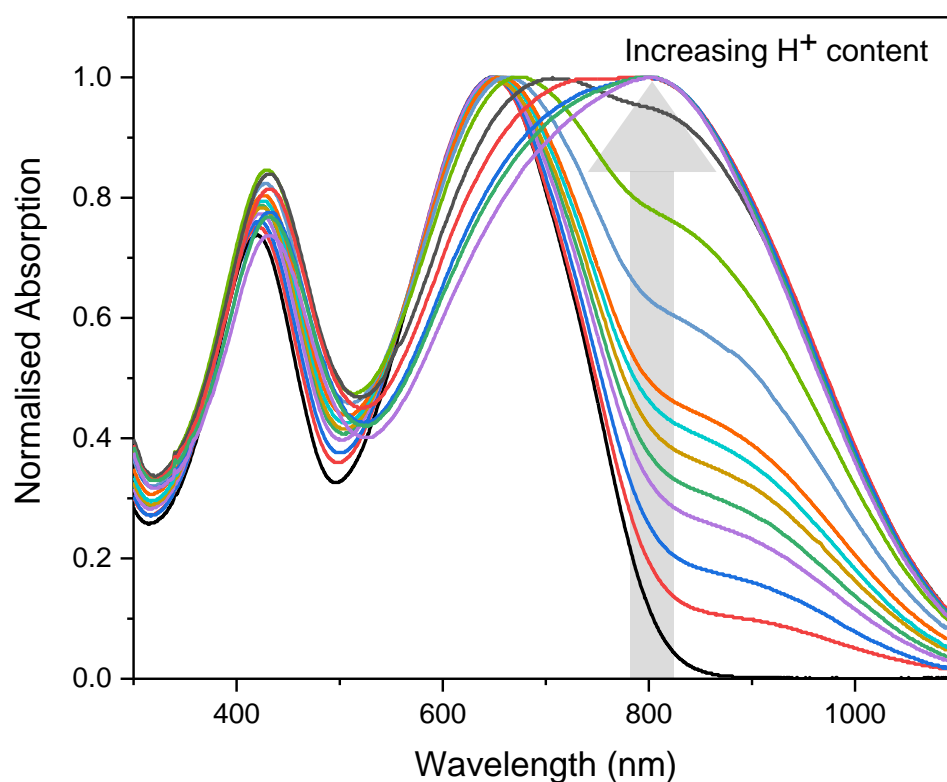
Table S2: Theoretical calculations performed on trimers of **PTBT**, **PTTPy** and **PTTPz** and determined using DFT-D3 at the level of B3LYP/def2-SVP. Octyl-dodecyl chains substituted for methyl groups for simplicity.

Polymer	HOMO (eV)	LUMO (eV)	$E_g$ (eV) <sup>a</sup>
PTBT	-4.77	-2.99	1.79
PTTPy	-4.84	-3.20	1.64
PTTPz	-4.95	-3.40	1.55

<sup>a</sup>LUMO - HOMO.

## 6) UV-Visible-Near IR Absorption Spectra

Figure S1: Normalised UV-visible-near IR absorption spectra of **PTTPz** in chloroform with increasing content of *p*-toluene sulfonic acid (0.001 M).



The stability of **PTTPz** in acid was tested after the content of *p*-toluene sulfonic acid (*p*-TSA) in a solution of the novel polymer **PTTPz** (in chloroform) was increased. This was in order to demonstrate whether one or both basic nitrogen sites of the pyridazine thiadiazole (PzT) unit can undergo protonation.

A stock solution of *p*-TSA (0.001 M) was firstly prepared in chloroform. A solution of **PTTPz** in chloroform was then prepared in a cuvette and the absorption spectrum was measured. The volume of acid was then gradually increased and the absorption spectrum after each successive addition was measured. Figure S1 shows the normalised UV-visible-near IR absorption spectra of **PTTPz** in chloroform with increasing content of *p*-toluene sulfonic acid (0.001 M).

The absorption spectra clearly demonstrate that **PTTPz** is influenced by the presence of acid. As the acid content is increased, the absorption maximum at ~648 nm develops a red-edge shoulder, which becomes increasingly more prominent with each successive addition of acid. The absorption onsets and maxima significantly red-shift and the absorption profile broadens as the initial 0-0 peak merges with the new red-edge shoulder. A similar effect was observed by E. Ratcliff *et al.* when increasing the content of *p*-TSA in a solution of d-DTS(PTT<sub>2</sub>)<sub>2</sub> (a PyT-based small molecule) in chloroform.<sup>5</sup>

With **PTTPz**, an absorption maximum of ~ 800 nm is achieved, however with further addition of acid, this can red shift by ~ 40 nm more, and then a cap is reached. It was thought that the pKa of the acid may have inhibited further protonation of the second nitrogen site, thus the stronger trifluoromethane sulfonic acid (TFMSA) was also tested. However, after the gradual addition of 0.1 mL of 0.01 M TFMSA, the polymer decomposed.

Based on these observations, it is likely that **PTTPz** has only been singly protonated and that the protonation of both basic nitrogen sites of the polymer, is unlikely achievable.

## 7) Supplementary References

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2. T. Nakanishi, Y. Shirai, & L. Han, *J. Mater. Chem. A.* 2015, **3**, 4229–4238.
3. Y. Sun, S.-C. Chien, H.-L. Yip, Y. Zhang, K.-S. Chen, D. F. Zeigler, F.-C. Chen, B. Lin & A. K.-Y. Jen, *J. Mater. Chem.* 2011, **21**, 13247–13255.
4. S. Grimme, J. Antony, S. Ehrlich & H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
5. E. L. Ratcliff, R. C. Bakus II, G. C. Welch, T. S. van der Poll, A. Garcia, S. R. Cowan, B. A. MacLeod, D. S. Ginley, G. C. Bazan & D. C. Olson, *J. Mater. Chem. C.* 2013, **1**, 6223–6234.