

Supplementary Material (ESI) for Chemical Communications

## **Anthracene-based donor/acceptor low band gap polymers for application in solar cells**

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### **Experimental Section**

**Materials:** 2,6-Dibromo-9,10-anthraquinone,<sup>1</sup> 4,7-bis-(5-bromo-thiophen-2-yl)-benzo[1,2,5]thiadiazole **5**,<sup>2</sup> 4,7-bis-(5-bromo-thiophen-2-yl)-5,6-bis-octyloxy-benzo[1,2,5]thiadiazole **6**<sup>3</sup> and 4,7-bis-(5'-bromo-[2,2']bithiophenyl-5-yl)-5,6-bis-octyloxy-benzo[1,2,5]thiadiazole **7**<sup>4</sup> were prepared according to literature procedures. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under inert nitrogen atmosphere. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile (High performance liquid chromatography (HPLC) grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere, then stored over molecular sieves 3Å.

**Measurements.** Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500 MHz NMR spectrometers at 22 °C in chloroform-*d*

solutions with TMS as the internal standard. Polymer solutions in 1,2,4-trichlorobenzene at 100 °C were used as samples for GPC analysis. The GPC curves were obtained by the RI-detection method, which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Elemental analyses were carried out by the Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. UV–visible absorption spectra were measured by Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. The absorbance of polymers was measured in solution in chloroform (spectrophotometric grade) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma-Aldrich. Samples of pristine polymer thin films for UV–visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm<sup>-3</sup> polymer solutions in chloroform (HPLC grade); and the measurements were carried out at ambient temperature. Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25±2 °C. 10 ml of tetrabutylammonium hexafluorophosphate solution in acetonitrile (0.1 mol dm<sup>-3</sup>) was used as the electrolyte solution. A three electrode system was used consisting of an Ag/Ag<sup>+</sup> reference electrode (silver wire in 0.01 mol dm<sup>-3</sup> silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm-diameter smooth platinum disc, area=3.14×10<sup>-2</sup> cm<sup>2</sup>), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm<sup>3</sup> of polymer solutions in chloroform (HPLC grade) (1 mg cm<sup>-3</sup>) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation.<sup>5</sup>

Photovoltaic devices were fabricated onto pre-patterned ITO glass substrates (20 Ohms/square) that were supplied by Ossila Limited. The protective resist covering the ITO was removed by being placed in a 10% sodium hydroxide solution for 5 minutes. A 20 - 30nm thick layer of PEDOT:PSS (HC Starck Clevios P AI4083) was spin-coated onto the ITO substrates that were then transferred to a hot-plate held at a temperature of 125°C. The coated substrates were then

transferred to a nitrogen glovebox where they were given a further thermal anneal at 125°C for 5 minutes.

We have explored a range of fabrication protocols to optimise the efficiency of devices based on our polymeric materials. In particular, we have explored the role of casting solvent, film thickness and polymer-fullerene ratio. To fabricate a device, the polymer of interest was dissolved with PC<sub>70</sub>BM at a relative concentration ranging between 1:2 and 1:4 polymer:PC<sub>70</sub>BM by mass. Polymer solutions were produced at a concentration of 12 mg/ml using the solvents dichlorobenzene (DCB), chlorobenzene (CB) or chloroform. Solutions were heated to 70°C for 60 hours to fully solubilise both components before being filtered using a 0.45µm PTFE filter. After the solutions were cooled, they were spin-coated onto the PEDOT:PSS coated ITO to produce a film having a thickness between 55nm-75nm. To create a device, a cathode consisting of calcium (10 nm) and aluminium (100 nm) was thermally evaporated on top of the active layer in a vacuum of less than 10<sup>-6</sup> mbar. Finally, devices were encapsulated using a UV-curable epoxy and glass slide. To characterise devices, J – V characteristics were recorded when devices were illuminated using a Newport 92251A-1000 AM1.5 solar simulator with NREL certified silicon reference cell.

All reactions were carried out under inert nitrogen or argon atmosphere.

#### *2,6-Dibromo-9,10-bis(4-(dodecyloxy)phenyl)-9,10-dihydroanthracene-9,10-diol 2*

To a solution of 1-bromo-4-(dodecyloxy)benzene (2.8 g, 8.2 mmol) in THF (50 ml) was added *n*-BuLi (3.8 ml, 5.56 mmol, 1.6 M in pentane) at -78 °C. After 3 hours, 2,6-dibromoanthracene-9,10-dione (1 g, 2.73 mmol) was added. The resulting mixture was allowed to warm to room temperature slowly. After stirring overnight, the mixture was poured into water (200 ml) and extracted with diethyl ether (2 × 200 ml). The organic layer was washed with brine (200 ml) then dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the product was purified using column chromatography (ethyl acetate/ petroleum ether (1/10) (v/v)) to obtain **2** as a yellow solid (5.2 g, 76.2% yield). The product gave a single spot on TLC (R<sub>f</sub> = 0.39) (silica-gel plates - ethyl

acetate/ petroleum ether (1/10) (v/v)). Mass (EI); (m/z): 890.2 ( $M^+$ ).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) ( $\delta_{\text{H}}$ /ppm) 8.03 (s, 2H), 7.77 (d,  $J = 8.27$  Hz, 2H), 7.58 (dd,  $J = 8.30, 1.58$  Hz, 2H), 6.60-6.31 (m, 4H), 6.33-6.07 (m, 4H), 3.69 (s, 4H), 1.67 (m, 4H), 1.50-1.14 (m, 36H), 0.90 (t,  $J = 6.78$  Hz, 6H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) ( $\delta_{\text{C}}$ /ppm) 142.91, 139.77, 130.88, 129.14, 128.36, 128.01, 122.12, 113.43, 74.45, 68.0, 31.93, 29.69, 29.65, 29.62, 29.47, 29.37, 29.23, 26.03, 22.71, 14.14. Anal. Calcd. for  $\text{C}_{50}\text{H}_{66}\text{O}_4\text{Br}_2$ : C, 67.41; H, 7.47; Br, 17.94. Found: C, 67.05; H, 7.65; Br, 17.89.

#### *2,6-Dibromo-9,10-bis(4-(dodecyloxy)phenyl)anthracene 3*

A mixture of 2,6-dibromo-9,10-bis(4-(dodecyloxy)phenyl)-9,10-dihydroanthracene-9,10-diol **2** (13.5 g, 15.20 mmol), KI (21.8 g, 131.48 mmol),  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  (15.4g, 175.4 mmol) and acetic acid (152 ml) was heated at reflux for 40 min. The precipitate was collected and dissolved in dichloromethane (DCM). The organic solution was washed with brine then dried over anhydrous  $\text{MgSO}_4$ . After solvent removal, the residue was purified by column chromatography on silica gel with petroleum ether:DCM (4:1, v:v) and then recrystallization from hexane to afford the target product (8.3 g, 63.4 % yield) as light yellow crystals. The product gave a single spot on TLC ( $R_{\text{f}} = 0.45$ ) (silica-gel plates - petroleum ether: DCM (4:1) (v/v)). Mass (EI); (m/z): 856.3 ( $M^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta_{\text{H}}$ /ppm) 7.89 (d,  $J = 1.85$  Hz, 2H), 7.61 (d,  $J = 9.32$  Hz, 2H), 7.37 (m, 6H), 7.15 (d,  $J = 8.63$  Hz, 4H), 4.13 (t,  $J = 6.50$  Hz, 4H), 1.92 (m, 4H), 1.46 (m, 36H), 0.91 (t,  $J = 6.52$  Hz, 6H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) ( $\delta_{\text{C}}$ /ppm) 158.97, 136.59, 132.21, 131.28, 129.47, 129.19, 129.05, 128.5, 128.82, 120.05, 120.05, 114.66, 68.19, 31.96, 29.72, 29.67, 29.50, 29.43, 29.40, 26.20, 22.73, 14.16; Anal. Calcd. for  $\text{C}_{50}\text{H}_{64}\text{O}_2\text{Br}_2$ : C, 70.09; H, 7.53; Br, 18.65. Found: C, 70.26; H, 7.68; Br, 18.66.

#### *2,6-Bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,10-bis(4-(dodecyloxy)phenyl) anthracene*

**4**

2,6-Dibromo-9,10-bis(4-(dodecyloxy)phenyl)anthracene **3** (3 g, 3.50 mmol), bis(pinacolato) diboron (4.33 g, 12.2 mmol), potassium acetate (2.06 g, 20.96 mmol) and  $\text{Pd}(\text{dppf})\text{Cl}_2$  (0.17 g, 0.022 mmol) in DMF (42 ml) was heated to 100 °C for 36 h. The reaction mixture was cooled to room temperature, then poured into  $\text{H}_2\text{O}$  (100 ml) and extracted with diethyl ether ( $3 \times 100$  ml).

The organic phases were combined, then washed with H<sub>2</sub>O (5 × 100 ml) and dried over MgSO<sub>4</sub>.

The crude product was purified *via* recrystallisation; the crude product was dissolved in the minimum amount of diethyl ether and then precipitated into hot methanol (which had been passed through a basic alumina column beforehand). The product was obtained as a light yellow crystal.

(2.3 g, 69.1 % yield). Mass (EI); (m/z): 950.5 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ<sub>H</sub>/ppm) 8.32 (s, 2H), 7.70 (d, J = 7.00 Hz, 2H), 7.66 (d, J = 7.00 Hz, 2H), 7.40 (d, J = 8.54 Hz, 4H), 7.17 (d, J = 8.59 Hz, 4H), 4.17 (t, J = 6.59 Hz, 4H), 1.99-1.88 (m, 4H), 1.66-1.55 (m, 6H), 1.50-1.26 (m, 54H), 0.92 (t, J = 6.78 Hz, 6H). <sup>13</sup>CNMR (CDCl<sub>3</sub>) (δ<sub>C</sub>/ppm) 158.49, 137.76, 135.66, 132.58, 131.42, 130.77, 130.25, 128.80, 126.26, 114.40, 83.75, 68.21, 31.95, 29.72, 29.67, 29.55, 29.51, 29.39, 26.21, 24.82, 22.72, 14.15.; Anal. Calcd. for C<sub>62</sub>H<sub>88</sub>O<sub>6</sub>B<sub>2</sub>: C, 78.30; H, 9.33. Found: C, 77.77; H, 9.58.

*Poly(9,10-bis(4-(dodecyloxy)phenyl)anthracene-2,6-diyl-alt-(4,7-dithiophen-2-yl)-2',1',3'-benzothiadiazole-5,5-diyl]* **PPATBT**

To a solution of 2,6-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,10-bis(4-(dodecyloxy)phenyl)anthracene **4** (0.35 g, 0.367 mmol) and 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.1683 g, 0.367 mmol) in dry toluene (9 ml) was added a 20 % w/w aqueous solution of tetraethylammonium hydroxide (2.1 ml, 2.85 mmol) and the mixture was degassed. To this mixture was added Pd(AcO)<sub>2</sub> (6.3 mg, 0.028 mmol) and tri-*o*-tolylphosphine (17.2 mg, 0.0565 mmol) and the mixture was degassed then heated to 90 °C for 24 h. After cooling, the polymer was end-capped with the addition of 1-bromobenzene (0.1 ml, 0.94 mmol) and heated to 90 °C for 1 h. After cooling to room temperature, phenyl boronic acid (0.15 g, 1.23 mmol) was added and again the reaction was heated to 90 °C for 3 h. The reaction mixture was cooled to room temperature, then dissolved in CHCl<sub>3</sub> (200 ml) and to this solution was added an ammonium hydroxide solution (28% in H<sub>2</sub>O, 50 ml) followed by stirring overnight. Then, the organic layer was separated and washed with distilled water. The organic layer was concentrated to about 10 ml and poured into methanol (300 ml). The resulting mixture was stirred overnight and filtered through a membrane filter. The solid obtained was cleaned using Soxhlet extraction with solvents in order:

methanol, acetone, hexane, toluene, chloroform and finally chlorobenzene. The toluene, chloroform and chlorobenzene fractions were concentrated to about 50 ml and then poured into degassed methanol (200 ml). The resulting mixtures were stirred overnight and the solids collected by filtration as purple powders. Toluene fraction (128 mg, 35%); chloroform fraction (162 mg, 44.2%) and chlorobenzene fraction (45 mg, 12 %). GPC: toluene fraction  $M_n = 3000$ ,  $M_w = 3800$ ; chloroform fraction  $M_n = 3500$ ,  $M_w = 4900$ ; chlorobenzene fraction  $M_n = 7800$ ;  $M_w = 9100$ .  $^1\text{H}$  NMR of the toluene fraction ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100\text{ }^\circ\text{C}$ ) ( $\delta_{\text{H}}/\text{ppm}$ ) 8.07 (d,  $J = 3.86$  Hz, 2H), 7.84 (s, 2H), 7.66 (d,  $J = 7.29$  Hz, 4H), 7.44 (d,  $J = 6.37$  Hz, 2H), 7.37 (m, 2H), 7.29 (d,  $J = 7.34$  Hz, 4H), 7.19 (d,  $J = 7.81$  Hz, 4H), 4.15 (t,  $J = 5.92$  Hz, 4H), 1.94-1.84 (m, 4H), 1.60-1.18 (m, 36H), 0.85 (t,  $J = 6.51$  Hz, 6H).

*Poly(9,10-bis(4-(dodecyloxy)phenyl)anthracene-2,6-diyl-alt-(5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,5-diyl) PPATBT-8*

To a solution of 2,6-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,10-bis(4-(dodecyloxy)phenyl)anthracene **4** (0.35 g, 0.367 mmol) and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (0.2625 g, 0.367 mmol) in dry toluene (9 ml) was added a 20 % w/w aqueous solution of tetraethylammonium hydroxide (2.1 ml, 2.85 mmol) and the mixture was degassed.  $\text{Pd}(\text{AcO})_2$  (6.3 mg, 0.028 mmol) and tri-*o*-tolylphosphine (17.2 mg, 0.0565 mmol) were then added and the mixture degassed, then heated to  $90\text{ }^\circ\text{C}$  for 24 h. After cooling, the polymer was end-capped with the addition of 1-bromobenzene (0.1 ml, 0.94 mmol) and heating the mixture to  $90\text{ }^\circ\text{C}$  for 1 h. After cooling to room temperature, phenyl boronic acid (0.15 g, 1.23 mmol) was added and again the reaction was heated to  $90\text{ }^\circ\text{C}$  for 3 h. The reaction mixture was cooled to room temperature, then dissolved in  $\text{CHCl}_3$  (200 ml) and to this solution was added an ammonium hydroxide solution (28% in  $\text{H}_2\text{O}$ , 50 ml) followed by stirring overnight. The organic layer was separated and washed with distilled water, concentrated to about 10 ml and poured into methanol 300 ml. After stirring overnight, the polymer was filtered through a membrane filter and was cleaned using Soxhlet extraction with solvents in order: methanol, acetone, hexane, toluene and

chloroform. The toluene and chloroform fractions were concentrated to about 50 ml and then poured into degassed methanol (200 ml). The result mixtures were stirred overnight and the polymer fractions collected by filtration as purple powders. Toluene fraction, (136 mg, 29.5 %) and chloroform (250 mg, 54 %). GPC: toluene fraction, Mn= 9100, Mw= 12600; chloroform fraction Mn= 25000, Mw= 33900. <sup>1</sup>H NMR of the toluene fraction (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 °C) (δ<sub>H</sub>/ppm) 8.43 (s, 2H), 8.08 (bs, 4H), 7.79 (m, 2H), 7.67 (d, *J* = 8.98 Hz, 2H), 7.45 (d, *J* = 7.73 Hz, 4H), 7.17 (d, *J* = 8.18 Hz, 4H), 4.14 (bs, 8H), 1.99-1.81 (m, 8H), 1.62-1.09 (m, 56H), 0.93-0.74 (m, 12H).

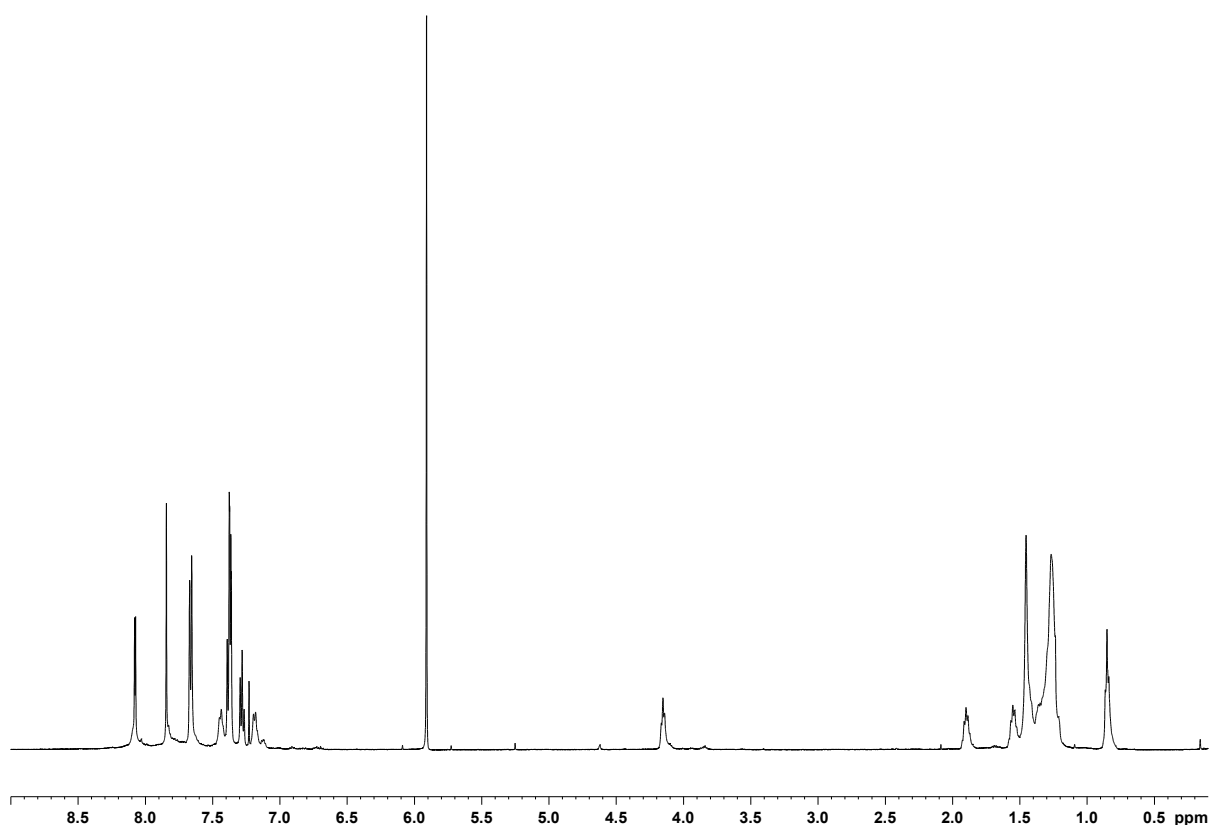
*Poly(9,10-bis(4-(dodecyloxy)phenyl)-anthracene-2,6-diyl-alt-(5,6-bis(octyloxy)-4,7-di(2,2'-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)-5,5-diyl) PPAT2BT-8*

To a solution of 2,6-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,10-bis(4-(dodecyloxy)phenyl)anthracene **4** (0.200 g, 0.210 mmol) and 4,7-bis-(5'-bromo-[2,2']bithiophenyl-5-yl)-5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (0.185 g, 0.210 mmol) in dry toluene (8 ml) was added a 20 % w/w aqueous solution of tetraethylammonium hydroxide (1.3 ml, 1.76 mmol) and the mixture was degassed. To this mixture was added Pd(AcO)<sub>2</sub> (3.3 mg, 0.015 mmol) and tri-*o*-tolylphosphine (9 mg, 0.0295 mmol) and the mixture was degassed then heated to 95 °C for 3 h. After cooling, the polymer was end-capped with the addition of 1-bromobenzene (0.1 ml, 0.94 mmol) and heated to 90 °C for 1 h. After cooling to room temperature, phenyl boronic acid (0.120 g; 0.984 mmol) was added and again the reaction was heated to 90 °C for 3 h. The reaction mixture was cooled to room temperature, then dissolved in CHCl<sub>3</sub> (200 ml) and to this solution was added an ammonium hydroxide solution (28% in H<sub>2</sub>O, 50 ml) followed by stirring overnight. Then, the organic layer was separated and washed with distilled water. The organic layer was concentrated to about 50 ml and poured into methanol (300 ml). The resulting mixture was stirred overnight and filtered through a membrane filter. The solid obtained was cleaned using Soxhlet extraction with solvents in order: methanol, acetone, hexane, toluene and chloroform. The chloroform fraction was concentrated to about 50 ml and then poured into methanol (200 ml). The resulting mixture was stirred overnight and the solid collected by filtration to afford the product as dark purple (0.044 g ,

yield 15%). GPC: chloroform fraction ( $M_n = 15.400$ ), ( $M_w = 19.100$ );  $^1\text{H}$  NMR of the chloroform fraction ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100\text{ }^\circ\text{C}$ ) ( $\delta_{\text{H}}/\text{ppm}$ ) 8.47 (s, 2H), 7.95 (bs, 2H), 7.80 (m, 2H), 7.65 (m, 2H), 7.55 (m, 2H), 7.40 (m, 4H), 7.3 – 7.05 (m, 8H), 4.05 (bm, 8H), 1.99-1.81 (m, 8H), 1.60-1.20 (m, 56H), 0.93-0.80 (m, 12H). Anal. Calcd. for  $\text{C}_{88}\text{H}_{106}\text{N}_2\text{O}_4\text{S}_5$ : C, 74.64; H, 7.54; N, 1.98; S, 11.32. Found: C, 72.85; H, 7.20; N, 1.60; S, 9.10.

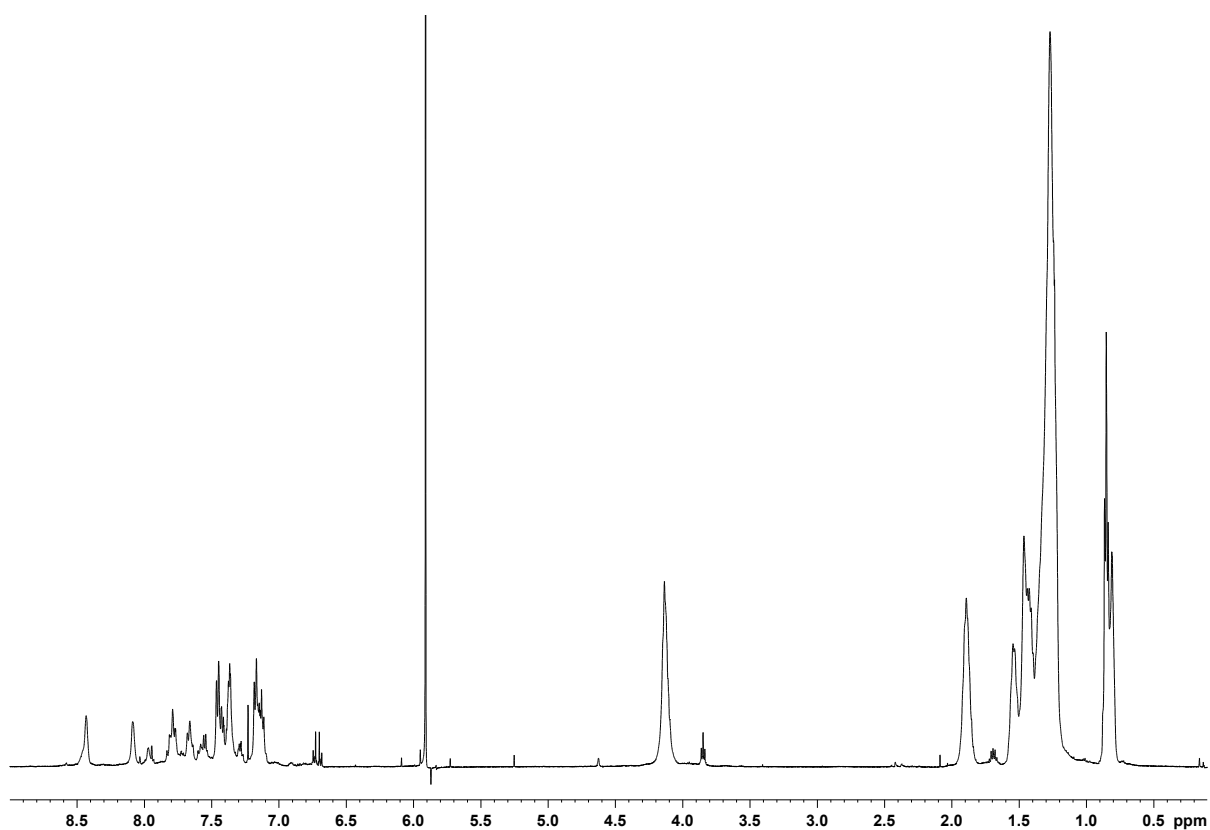
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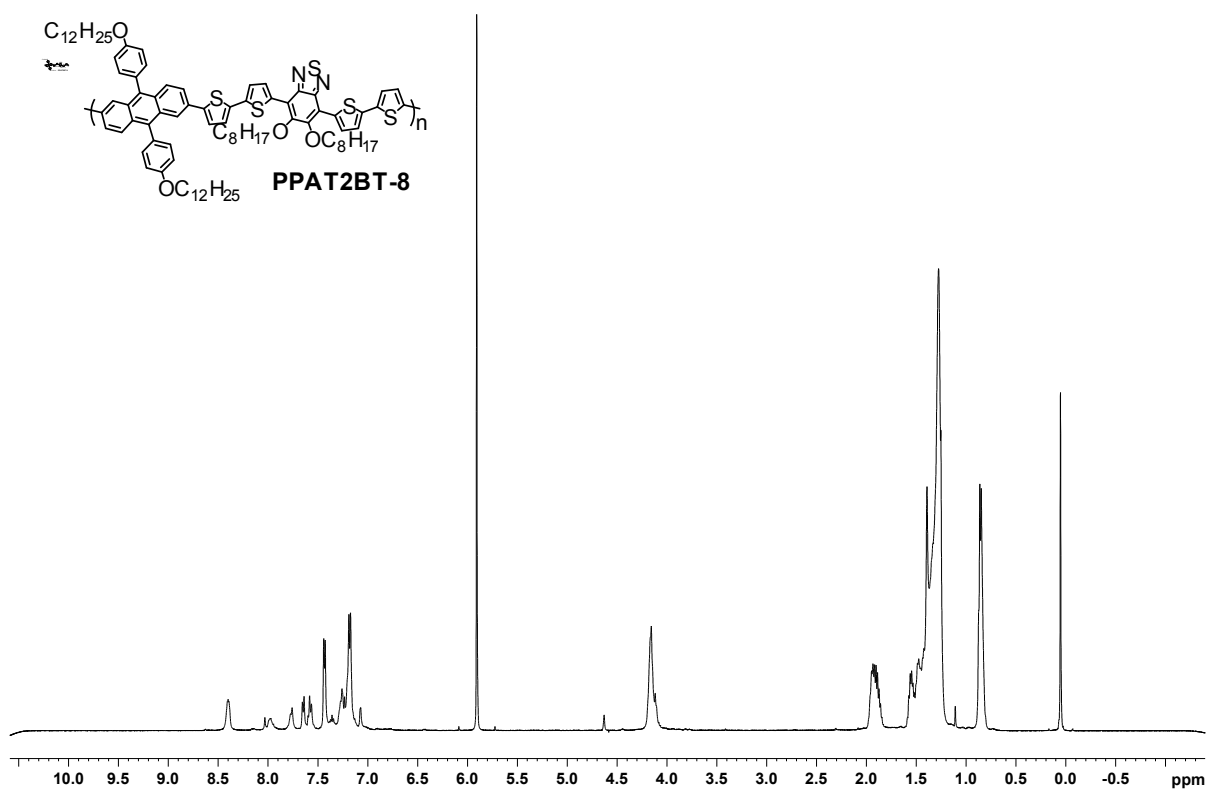


**Figure S1.**  $^1\text{H}$  NMR spectrum of the toluene fraction of PPATBT in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $100\text{ }^\circ\text{C}$ .





**Figure S2.** <sup>1</sup>H NMR spectrum of the toluene fraction of **PPATBT-8** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 100 °C.



**Figure S3.** <sup>1</sup>H NMR spectrum of the chloroform fraction of **PPAT2BT-8** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 100 °C.