# **Supporting information**

# Metal-Free Polymerization: Synthesis and Properties of Fused Benzo[1,2-b:4,5-b']bis[b]benzothiophene (BBBT) polymers

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#### 1. Materials and methods

All chemicals were purchased from commercial suppliers and used as received unless otherwise specified. Column chromatography was carried out with silica gel for flash chromatography from VWR Scientific. Microwave experiments were performed in a Biotage Initiator V 2.3. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Model 400 spectrometer and high temperature <sup>1</sup>H NMR was recorded on a Bruker Model 500 spectrometer. Number-average (Mn) and weight-average (Mw) molecular weights were determined with an Agilent Technologies 1200 series GPC in chlorobenzene at 80°C, using two PL mixed B columns in series, and calibrated against narrow weight-average dispersity (Dw < 1.10) polystyrene standards. The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q50 under a continuous nitrogen purge of 60 mL/min. The samples were heated from room temperature to 800°C with a uniform heating rate of 10°C/min. UV-vis-NIR absorption spectra were recorded on a UV- 1601 Shimadzu UV-vis spectrometer. Photoelectron spectroscopy in air (PESA) measurements were recorded with a Riken Keiki Model AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Electron affinity values were obtained using the following equation:  $EA = (IP-E_{opt}) eV$ .



Figure S1: The GPC data of BBBT-P.



MW Averages										
Peak No	Мр	Mn	Mw	Mz	Mz+1	Mv	PD			
1	57549	40324	80326	157164	261910	72060	1.99201			





Figure S3: The GPC data of **BBBT-BBBT**.

## 3. TGA data



Figure S4: the TGA data of **BBBT-P**.



Figure S5: the TGA data of **BBBT-N**.



Figure S6: the TGA data of **BBBT-BBBT**.

## 4. Temperature-controlled UV-vis absorption measurements





Figure S7. Temperature-dependent UV-vis-NIR absorption spectra of the polymers in chlorobenzene.

#### 5. DFT calculation



Figure S8: Pictorial representation of hole and electron wavefunctions of **BBBT-P** fused oligomers as determined at TD-OT- $\omega$ B97XD/6-31G\*\* level of theory.



Figure S9: Pictorial representation of hole and electron wavefucntions of **BBBT-N** fused oligomers as determined at TD-OT- $\omega$ B97XD/6-31G\*\* level of theory.





Figure S10: Pictorial representation of hole and electron wavefucntions of B**BBT-BBBT** fused oligomers as determined at TD-OT- $\omega$ B97XD/6-31G\*\* level of theory.

Table S1: Calculated HOMO, LUMO, HOMO-LUMO gap (HLG), and lowest excitation energy (S1) values (in eV) obtained at OT- $\omega$ B97XD/6-31G\*\* level of theory. The lowest excitation energy values are obtained using TD- OT- $\omega$ B97XD/6-31G\*\* level of theory.

	HOMO	LUMO	HLG	<b>S1</b>
BBBT-P	-5.36	-2.97	2.39	1.66
BBBT-N	-5.22	-2.96	2.26	1.62
BBBT-				
BBBT	-5.44	-2.81	2.63	1.99

#### 6. Experimental details



PO<sup>[S1]</sup>, NO<sup>[S2]</sup> and BBBTI <sup>[S3]</sup> were synthesized according to the literature.

#### **BBBT-P**

A microwave vial was charged with **PO** (47.51mg, 0.055 mmol), **BBBTI** (60.76 mg, 0.055 mmol), p-toluene sulfonic acid monohydrate (2.85 mg, 0.017 mmol). The vial was sealed and dry degassed toluene (1.2 mL) injected into the vial. The reaction was heated at 120°C for 22 hours. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, and hexane dichloromethane and chloroform. The chloroform fraction was collected and reduced under vacuum and the polymer precipitated into methanol. The polymer was filtered and dried, 93 mg, Yield: 87 %.

<sup>1</sup>H NMR (400 MHz, TCE-D<sub>2</sub>, 403K):  $\delta = 9.87$  (broad), 9.11(broad), 8.10 (broad), 7.15 (broad), 4,24-3.88(multi), 2.27-0.84(multi).

GPC (chlorobenzene, 80 °C): Mn= 14.79 kDa, Mw= 93.01 kDa, PDI = 6.29.

#### **BBBT-N**

A microwave vial was charged with **NO** (27.02 mg, 0.047 mmol), **BBBTI** (51.80 mg, 0.047 mmol), p-toluene sulfonic acid monohydrate (3.3 mg, 0.019 mmol). The vial was sealed and dry degassed toluene (1.2 mL) injected into the vial. The reaction was heated at  $120 \text{ }_{\circ}\text{C}$  for 3 days. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, and hexane dichloromethane and chloroform. The chloroform fraction was collected and reduced under vacuum and the polymer precipitated into methanol. The polymer was filtered and dried, 67 mg, Yield: 85 %.

<sup>1</sup>H NMR (400 MHz, TCE-D<sub>2</sub>, 403K):  $\delta$  =9.89 (broad), 9.10 (broad), 8.61 (broad), 7.73-7.19 (broad), 6.81(broad), 4.43-3.69(multi), 2.47-0.82 (multi). GPC (chlorobenzene, 80 °C): Mn= 40.32 kDa, Mw= 80.33 kDa, PDI= 1.99

#### **BBBT-BBBT**

A solution of **BBBTI** (61.06 mg, 0.0554 mmol) in toluene (1.0 mL) was degassed for 10 mins at room temperature. Hexaethyltriaminophosphine (34 ul) was slowly added to the reaction mixture with a micro syringe, then allowed to warm to reflux for 2 days. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, and hexane dichloromethane and chloroform. The chloroform fraction was collected and reduced under vacuum and the polymer precipitated into methanol. The polymer was filtered and dried, 48 mg, Yield: 79 %.

<sup>1</sup>H NMR (400 MHz, TCE-D<sub>2</sub>, 403K):  $\delta = 10.02$  (broad), 8.61(broad), 8.12 (broad), 7.78-7.59 (broad), 4.40-3.11(multi), 2.07-0.76(multi).

GPC (chlorobenzene, 80 °C): Mn = 18.42 KDa, Mw = 35.11 KDa, PDI =1.91.



#### <sup>1</sup>H NMR Figures of Polymers

Figure S11: <sup>1</sup>H NMR of polymer **BBBT-P** in TCE-D<sub>2</sub> at 403K.



Figure S12: <sup>1</sup>H NMR of polymer BBBT-N in TCE-D<sub>2</sub> at 403K.



Figure S13: <sup>1</sup>H NMR of polymer **BBBT-BBBT** in TCE-D<sub>2</sub> at 403K.

## References

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