# **Supplementary Information**

# Preparing DNA-Mimicking Multi-Line Nanocaterpillars via In Situ Nanoparticlisation of Fully Conjugated Polymers

In-Hwan Lee,<sup>a</sup> Pitchamuthu Amaladass,<sup>a</sup> Inho Choi,<sup>a</sup> Victor W. Bergmann,<sup>b</sup> Stefan A. L. Weber<sup>b</sup> and Tae-Lim Choi<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, Seoul National University, Seoul, 08826, Korea <sup>b</sup>Max Planck Institute for Polymer Research, 55128 Mainz, Germany

E-mail: tlc@snu.ac.kr

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#### **General experimental considerations**

NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for <sup>1</sup>H, 125 MHz for <sup>13</sup>C) and Agilent 400-MR DD2 Magnetic Resonance System (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C). THF Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2414 refractive index detector and 2489 UV detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson). Flow rate was 1.0 mL/min and temperature of column was maintained at 35 °C. Samples were diluted in 0.001-0.005 wt% by THF and filtered with a 0.20  $\mu$ m PTFE filter before injection into the GPC. UV/Vis spectra were obtained by Jasco Inc. UV-vis Spectrometer V-650. Powder X-ray diffraction (XRD) was performed by the National Instrumentation Center for Environmental Management (NICEM) at SNU using D8 Discover with GADDS (Bruker, Germany). Dynamic light scattering (DLS) data were obtained by Malvern Zetasizer Nano ZS. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under N<sub>2</sub> gas at a scan rate of 10 °C/min with Q50 and Q10 model devices, respectively, from TA Instruments. Cyclic voltammetry (CV) measurements were carried out on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA). Sonication was carried out with Powersonic 410 model devices from Hwashin Tech operating at AC220V 50/60 Hz and 500 W.

#### Materials

Without additional notes, all reagents were commercially available and used without further purification. THF was distilled over sodium and benzophenone.

#### 1-Bromo-4-iodo-2,5-dihexyloxybenzene and 1-bromo-4-iodo-2,5-di(2-ethylhexyloxy)benzene

: These monomers were prepared by using the previously reported procedure.<sup>43</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses data are available in the previous literatures.<sup>43, S1</sup>

#### 2-Bromo-5-iodo-3-methylthiophene

: This monomer was prepared by slightly modified method from the previous literature.<sup>S2</sup>

#### General polymerization procedure

#### Syntheses of PPP-b-P3MT and PPP(EH)-b-P3MT

Two round-bottomed two-neck flasks were flame-dried under reduced pressure and cooled to room temperature. The dried flasks were backfilled with argon. 1-Bromo-4-iodo-2,5-dihexyloxybenzene (in case of PPP(EH), 1-bromo-4-iodo-2,5-di(2ethylhexyloxy)benzene) (1 equiv.) was placed in one of the flasks under argon flow. After addition of dry THF (0.10–0.14 M) into the flask, 1.3*M* i-PrMgCl-LiCl complex in THF (1 equiv.) was added, and the mixture was stirred for 1 h at room temperature (solution 1). Meanwhile, 2-bromo-5-iodo-3-methylthiophene (0.7, 1.6, and 2.5 equiv.) (in case of PPP(EH); 0.5, 0.9, and 1.3 equiv.) and naphthalene (internal standard) were placed in the other flask under argon flow. After addition of dry THF (0.1 M) into the flask, 1.3M i-PrMgCl-LiCl complex in THF (0.7, 1.6 and 2.5 equiv.) (in case of PPP(EH); 0.5, 0.9, and 1.3 equiv., respectively) was added, and the mixture was stirred for 30 min at 0 °C (solution 2). After completion of the preparation of Grignard reagent from 1-bromo-4-iodo-2,5-dihexyloxybenzene (in case of PPP(EH), 1-bromo-4-iodo-2,5-di(2-ethylhexyloxy)benzene), Ni(dppe)Cl<sub>2</sub> catalyst (1.4 mol%) (in case of PPP(EH), 1.0 mol% was used) was added in solution 1 under argon flow. Polymerization underwent for 1 h at room temperature, and aliquot of solution 1 was taken to check the  $M_n$  and PDI values of the first block, i.e. PPP (and PPP(EH)). At the same time, an aliquot of solution 2 was taken to check the efficiency of Grignard exchange reaction of 2-bromo-5-iodo-3-methylthiophene. To perform block copolymerization, solution 2 was transferred into solution 1 via a cannula, and the resulting solution was stirred for 1 h at room temperature. After completion of reaction, an aliquot was taken to check the conversion of Grignard reagent from 2-bromo-5-iodo-3-methylthiophene. Finally, the polymerization was quenched by the addition of 6N HCl (aq.) to the resulting solution, and it was diluted with MeOH resulting in the precipitates. The reddish or dark-purple precipitates were collected by filtration, and washed by H<sub>2</sub>O and MeOH, which was dried under ambient condition.

#### Synthesis of PPP-b-PT

Two round-bottomed two-neck flasks were flame-dried under reduced pressure and cooled to room temperature, which was repeated three times. The dried flasks were backfilled with Ar and evacuated three times, then 1-bromo-4-iodo-2,5-dihexyloxybenzene (1 eq.) was placed in one of the flasks under Ar. After adding dry THF (0.10-0.14 *M*) into the flask, *i*-PrMgCl-LiCl complex in THF (1 eq.) was added, and the mixture was stirred for 1-2 h at room temperature (solution **A**). 2,5-Dibromothiophene (0.7, 1.0, 1.3, 1.6 eq.) and naphthalene (internal standard) were placed in the other flask under Ar. After adding dry THF (0.1 *M*) into the flask, *i*-PrMgCl-LiCl complex in THF (0.7, 1.0, 1.3, 1.6 eq., respectively) was added, and the mixture was stirred for 2-3 h at room temperature (solution **B**). Ni(dppe)Cl<sub>2</sub> catalyst (1.4 mol%) was added in solution **A**. After stirring for 1-2 h, aliquot of solution **A** was taken to measure the  $M_n$  and PDI values of the 1<sup>st</sup> block. An aliquot of solution **B** was taken to check the conversion of Grignard exchange reaction. Solution **B** was transferred into solution **A** via a cannula, and the resulting solution was stirred for 1 h. An aliquot was taken to check the conversion of Grignard monomer for 2<sup>nd</sup> block. After that, the polymerization was quenched by the addition of 6*N* HCl (aq.) to the resulting mixture, and it was diluted with MeOH leading to the precipitates. The resulting reddish or dark-purple precipitates were collected by filtration, and washed by  $H_2O$  and MeOH, which was dried under ambient condition.

#### Synthesis of PPP and PPP(EH) homopolymers

: These polymers were prepared by the GRIM method from the previous literature.<sup>42</sup>  $M_n = 14.0 \text{ kg/mol}$ , PDI = 1.17 for PPP (THF SEC, PS standard)  $M_n = 17.9 \text{ kg/mol}$ , PDI = 1.11 for PPP(EH) (THF SEC, PS standard)

#### **Detailed experimental procedure**

#### Atomic Force Microscopy (AFM)

The atomic force microscopy experiments were performed with a thin film prepared by spin-coating one drop of the polymer solution (0.05-0.1 mg polymer/mL chloroform or dichlorometane, spinning rate = 3000-5000 rpm for 30-60 sec) on freshly prepared highly ordered pyrolytic graphite (HOPG) substrates. Multimode 8 and Nanoscope V controller (Veeco Instrument) were used for AFM imaging. AFM images were obtained on tapping mode using non-contact mode tips from Nanoworld (Pointprobe® tip, NCHR type) with spring constant of 42 N m<sup>-1</sup> and tip radius of  $\leq 8$  nm and 2 nm. For the high resolution AFM images, we also used a low-noise AFM, based on a Digital Instruments multimode AFM with a homebuilt AFM head, ARC2 Controller by Asylum and a Nanosensors SSS-NCH Cantilever.

#### **Transmission Electron Microscopy (TEM)**

The samples for TEM were prepared by drop-casting  $10 \,\mu$ L aliquot of the polymer solution (0.005 mg polymer/mL chloroform) onto a carbon coated copper grid which was placed on a piece of paper to get rid of excess solvent. This polymer thin film was dried in the clean desiccator. The images were obtained by JEM-2100 operating at 200 kV accelerating voltage with ORIUS-SC 600 CCD camera or ORIUS-SC 1000 CCD camera (Gatan, Inc.) in the National Centre for Inter-University Research Facility (NCIRF) at SNU.

#### **Cyclic Voltammetry (CV)**

Cyclic voltammetry (CV) measurement was carried out at the room temperature on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA) using an degassed acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M). Thin film was prepared by drop-casting 10  $\mu$ L aliquot of the polymer solution onto the glassy carbon electrode. Cyclic voltammogram was recorded using the polymer-coated working electrode and a reference electrode of Ag/Ag<sup>+</sup> (0.1 M AgNO<sub>3</sub> in acetonitrile) with a platinum wire counter electrode at a scan rate of 50 mV/s. The absolute energy level was obtained using ferrocene/ferrocenium as an internal standard. The oxidation potential of ferrocene was regarded as - 4.8 eV.



#### Figure S1. Synthetic scheme for PPP-b-PT and PPP(EH)-b-P3MT

\*Measured by THF size exclusion chromatography calibrated using polystyrene standards. <sup>†</sup>Estimated by gas chromatography–mass spectrometry.

### Figure S2. <sup>1</sup>H NMR spectra of PPP-*b*-P3MT and PPP(EH)-*b*-P3MT (CDCl<sub>3</sub>)





#### (a) PPP<sub>70</sub>-*b*-P3MT<sub>50</sub> (film)



#### (b) PPP<sub>70</sub>-*b*-P3MT<sub>115</sub> (film)



(c) PPP<sub>70</sub>-*b*-P3MT<sub>180</sub> (film)



(e) PPP(EH)-b-P3MT in chloroform at room temperature





(a) PPP<sub>70</sub>-*b*-P3MT<sub>50</sub>

PPP<sub>70</sub>-b-P3MT<sub>50</sub>

0.0004

0.0003

0.0002

0.0001

0.0000

-0.0001

0.0

0.3

0.6

0.9

Potential (V vs Ag/AgCI)

Current (A)

# (b) PPP<sub>70</sub>-*b*-P3MT<sub>115</sub>







	optical $E_{\rm g}$	HOMO*	LUMO <sup>†</sup>
РЗНТ	1.9 eV	-4.9 eV	-3.0 eV
РРР	3.4 eV	-5.3 eV	-1.9 eV
PPP70- <i>b</i> -P3MT50	2.0 eV	-5.5 eV	-3.5 eV
PPP70- <i>b</i> -P3MT115	2.0 eV	-5.4 eV	-3.4 eV
PPP70-b-P3MT180	1.9 eV	-5.3 eV	-3.4 eV

\*HOMO level = -4.8 - ( $E_{\text{ox,onset}}$  - Fc<sup>1/2</sup>), †LUMO level = HOMO level + optical  $E_g$ , where Fc<sup>1/2</sup> = 0.08



# Figure S5. Powder XRD patterns of PPP-b-P3MT, PPP-b-PT, PPP, P3MT, and PT





(c) PPP, P3MT, and PT





(a) PPP homopolymer

(b) PPP<sub>70</sub>-*b*-P3MT<sub>50</sub>





(e) Melting temperature  $(T_m)$ , crystallization temperature  $(T_c)$ , and melting enthalpy  $(\Delta H_m)$ 

	PPP	PPP70- <i>b</i> -P3MT50	PPP70-b-P3MT115	PPP70-b-P3MT180
$T_{\rm m}$ (2 <sup>nd</sup> cycle)	89 °C	94 °C	not observed	not observed
T <sub>c</sub> (1 <sup>st</sup> cycle)	30 °C	not observed	not observed	not observed
$\Delta H_{\rm m} \left( { m J/g}  ight)$	47	15	-	-
Corrected $\Delta H_{\rm m}$ (J/g)	47	19	-	-

Correction of melting enthalpy =  $\frac{\text{original melting enthalpy}}{\text{grams of 1st block PPP from 1 gram of PPP - b - P3MT}}$ 

Compared to melting enthalpy ( $\Delta H_m$ ) of PPP homopolymer,  $\Delta H_m$  of PPP-*b*-P3MTs decreased with increasing DP of P3MT. We believe that this is mainly caused by geometrical factor of nanostructures. In other words, core-shell type geometry of nanostructures prohibited effective crystallization of PPP shell in solid state thereby decreasing  $\Delta H_m$ . In addition, increasing DP of P3MT made this phenomenon more severe, thus losing  $\Delta H_m$  totally. Similarly, when we look at the literature, this phenomenon was also observed in multi-armed P3HT star polymers.<sup>S3</sup> Even though P3HT has good stacking ability in solid, when it became star polymers, it was not crystallized due to geometrical restriction.<sup>S3</sup>

#### Figure S7. DLS profiles of PPP-b-PT and PPP(EH)-b-P3MT

(a) PPP-*b*-PT (CHCl<sub>3</sub>, 20 °C)







PPP(EH)<sub>100</sub>-b-P3MT<sub>50</sub>

# Figure S8. AFM and TEM images of nanostructures from PPP-*b*-P3MT, PPP-*b*-PT, and PPP(EH)*b*-P3MT

(a) PPP-b-P3MT



50 nm

50 nm



## (b) PPP-*b*-PT



#### (c) PPP(EH)-b-P3MT







# Figure S9. Average length and height of nanostructures from PPP-b-P3MT, PPP-b-PT, PPP(EH)*b*-P3MT based on AFM images

(a) Measurement of NPs' length based on AFM images





#### (b) Measurement of NPs' height based on AFM images



(c) Average length and height of nanostructures from PPP-b-PT, PPP-b-P3MT, and PPP(EH)-b-P3MT based on AFM images

$$L_{n} = \frac{\sum_{i=1}^{n} N_{i} L_{i}}{\sum_{i=1}^{n} N_{i}} \qquad \qquad L_{w} = \frac{\sum_{i=1}^{n} N_{i} L_{i}^{2}}{\sum_{i=1}^{n} N_{i} L_{i}}$$

	PPP70- <i>b</i> -PT50	PPP70- <i>b</i> -PT70	PPP70- <i>b</i> -PT90	PPP70- <i>b</i> -PT115
Ln	84 nm	94 nm	127 nm	131 nm
$L_{ m w}$	96 nm	107 nm	148 nm	152 nm
$L_{\rm w}/L_{\rm n}$	1.14	1.14	1.17	1.16
Height (STDEV)	4.4 nm (0.8 nm)	6.1 nm (0.8 nm)	7.3 nm (1.0 nm)	7.3 nm (0.8 nm)

(L = length of nanorod, N = number of nanorods, n = 35-170)

	PPP70- <i>b</i> - P3MT50	PPP70- <i>b</i> - P3MT115	PPP70- <i>b</i> - P3MT180	PPP(EH)100- <i>b</i> -P3MT50	PPP(EH)100- <i>b</i> -P3MT90	PPP(EH)100- b-P3MT130
Ln	130 nm	246 nm	n.d.	179 nm	431 nm	n.d.
$L_{ m w}$	189 nm	361 nm	n.d.	239 nm	759 nm	n.d.
$L_{\rm w}/L_{\rm n}$	1.45	1.47	n.d.	1.34	1.76	n.d.
Height (STDEV)	6.6 nm (0.7 nm)	9.9 nm (1.7 nm)	11.2 nm (1.9 nm)	6.1 nm (0.7 nm)	7.8 nm (1.0 nm)	14.4 nm (2.3 nm)



Figure S10. AFM and TEM images for the mixture of NPs from PPP70-b-PT90 and PPP70-b-P3MT70



#### Figure S11. Stability test for NPs from PPP-b-P3MT against sonication and high temperature

(a) Size of NPs from PPP70-b-P3MT50 and PPP70-b-P3MT115 in toluene at various temperatures from 20 °C to 80 °C



(b) AFM images of NPs from  $PPP_{70}$ -*b*-P3MT<sub>115</sub> on HOPG after sonication in CHCl<sub>3</sub> and UV-vis spectra of NPs from  $PPP_{70}$ -*b*-P3MT<sub>115</sub> in CHCl<sub>3</sub> at room temperature after sonication



(c) TEM images of NPs from PPP<sub>70</sub>-*b*-P3MT<sub>50</sub> and PPP<sub>70</sub>-*b*-P3MT<sub>115</sub> on Cu/C TEM grid after sonicating in CHCl<sub>3</sub> for 15 and 60 minutes





### References

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