Supplementary Information

One-pot synthesis of nanocaterpillar structures via in situ nanoparticlization of fully conjugated poly(*p*-phenylene)-*block*-polythiophene

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General experimental

NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for ¹H, 125 MHz for ¹³C) and Agilent 400-MR DD2 Magnetic Resonance System (400 MHz for ¹H, 100 MHz for ¹³C). 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 μ m PTFE filter before injection into the GPC. UV/Vis spectra were obtained by Jasco Inc. UV-vis Spectrometer V-550 and 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. Multimode 8 and Nanoscope V controller (Veeco Instrument) were used for atomic force microscopy (AFM) imaging. Transmission electron microscopy (TEM) imaging was performed by using JEM-2100 (JEOL) in the National Center for Inter-University Research Facility (NCIRF) at SNU. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under N₂ 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, and degassed by argon bubbling for 10 minutes before using on polymerization.

1,4-Dibromo-2,5-dihexyloxybenzene

: This monomer was prepared by slightly modified method from the previous literature.^{S1 1}H NMR and ¹³C NMR analyses data are available in the previous literature.^{6a}

General polymerization procedure

1. Synthesis of PPP-*b*-PTs

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 1,4-dibromo-2,5-dihexyloxybenzene (1 mmol) was placed in one of the flasks under Ar. After adding dry and degassed THF (0.2 M, 5 ml) into the flask, 1.3 M *i*-PrMgCl.LiCl complex in THF (1 mmol) was added, and the mixture was stirred overnight at room temperature (solution **A**). 2,5-Dibromothiophene (0.4, 0.8, 1.0, 1.3 mmol) and biphenyl (internal standard) were placed in the other flask under Ar. After adding dry and degassed THF (0.1 M; 4, 8, 10, 13 ml, respectively) into the flask, 1.3 M *i*-PrMgCl.LiCl complex in THF (0.4, 0.8, 1, 1.3 mmol, respectively) was added, and the mixture was stirred for 2 hr at room temperature (solution **B**). After overnight stirring of solution **A**, Ni(dppe)Cl₂ catalyst (1.45 mol%, 0.0145 mmol) was added in solution **A**. After stirring for 1-2 hr, aliquot of solution **A** was taken to measure the M_n and PDI values of the 1st block. An aliquot of solution **B** was taken to check the Grignard exchange reaction. Solution **B** was transferred into solution **A** via a cannula, and the resulting solution was stirred for 1 hr. An aliquot was taken to check the conversion of 2nd block monomer. After that, the polymerization was quenched by adding 6N HCl(aq) to the solution. The polymer solution (or suspension) was diluted by chloroform, and successively washed by NH₄Cl (*aq*.) and H₂O. After concentrating the solution by evaporation, it was precipitated into MeOH. The resulting red and purple solids were collected by filtration, and washed by H₂O, MeOH, and acetone, and finally dried in vacuo.

2. Synthesis of PPP homopolymer

: This polymer was prepared by the GRIM method from the previous literatures.^{6a} : $M_n = 14.0 \text{ kg/mol}$, PDI = 1.17 (THF SEC, PS standard)

Detailed experimental procedures

1. 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 chlorobenzene, spinning rate = 3000 rpm for 30-60 sec) on highly ordered pyrolytic graphite (HOPG) substrates. All images were obtained on tapping mode using non-contact mode tips from Nanoworld (Pointprobe® tip, NCHR type) with spring constant of 42 N m⁻¹ and tip radius of ≤ 8 nm.

2. Transmission Electron Microscopy (TEM)

: The samples for TEM were prepared by drop-casting 10 μ L aliquot of the polymer solution (0.005 mg polymer/mL chlorobenzene) 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 at least for 2 hr. The images were obtained on JEM-2100 operating at 200 kV accelerating voltage, using the images acquired with a ORIUS-SC 600 CCD camera or a ORIUS-SC 1000 CCD camera (Gatan, Inc.).

3. Cyclic Voltammetry (CV)

: Cyclic voltammetry (CV) measurements were 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_4NPF_6 , 0.1 M). Thin film was prepared by drop-casting 10 µL 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⁺ (0.1 M AgNO₃ 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. ¹H NMR and ¹³C NMR spectra of PPP-*b*-PTs



Figure S2. UV-vis spectra of PPP and PPP-b-PTs

(a) PPP and PPP-*b*-PT (in chloroform and film state)

(b) PPP₇₀-*b*-PT₃₀_film





(c) PPP₇₀-*b*-PT₅₅_film



0.10-

(d) PPP₇₀-*b*-PT₇₀_film



(e) PPP₇₀-*b*-PT₉₀_film





Figure S4. TGA and DSC profiles of PPP-b-PTs





(b) TGA profiles of PPP₇₀-*b*-PT₉₀



(c) DSC profile of PPP homopolymer



(d) DSC profile of PPP₇₀-*b*-PT₃₀





(g) DSC profile of PPP₇₀-*b*-PT₉₀



(h) Melting temperature (T_m) , crystallization temperature (T_c) , and melting enthalpy (ΔH_m)

	РРР	PPP ₇₀ - <i>b</i> -PT ₃₀	PPP ₇₀ - <i>b</i> -PT ₅₅	PPP ₇₀ - <i>b</i> -PT ₇₀	PPP ₇₀ - <i>b</i> -PT ₉₀
$T_{\rm m}(2^{\rm nd}{ m cycle})$	89 °C	88 °C	86 °C	87 °C	82 °C
$T_{\rm c}$ (1 st cycle)	30 °C	38, 58 °C	42 °C	46 °C	40 °C
$\Delta H_{\rm m} \left({\rm J}/{\rm g} \right)$	47	30	16	11	6
Corrected $\Delta H_{\rm m}$ (J/g)	47	34	20	14	9

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

Figure S5. AFM and TEM images of nanostructures from PPP-*b*-PTs

(a) PPP₇₀-*b*-PT₃₀



(b) PPP₇₀-*b*-PT₅₅



(c) PPP₇₀-*b*-PT₇₀









Figure S6. Average length of nanostructures from PPP-b-PTs based on AFM images

(a) PPP₇₀-*b*-PT₅₅

(b) PPP₇₀-*b*-PT₇₀

(c) PPP₇₀-*b*-PT₉₀



	PPP ₇₀ - <i>b</i> -PT ₅₅	PPP ₇₀ - <i>b</i> -PT ₇₀	PPP ₇₀ - <i>b</i> -PT ₉₀
$L_{ m n}$	76 nm	102 nm	121 nm
$L_{ m w}$	86 nm	128 nm	140 nm
$L_{ m w}/L_{ m n}$	1.13	1.25	1.16
Standard deviation	28 nm	52 nm	49 nm

$\sum_{i=1}^{n} N_i L_i$	$\sum_{i=1}^{n} N_i L_i^2$
$L_n = \frac{\sum_{i=1}^n N_i}{\sum_{i=1}^n N_i}$	$L_w = \frac{1}{\sum_{i=1}^n N_i L_i}$

(L = length of nanorod, N = number of nanorods, n = 30 - 50)

Figure S7. Average height of nanostructures from PPP-b-PTs based on AFM images

(a) PPP₇₀-*b*-PT₃₀

(b) PPP₇₀-*b*-PT₅₅



(c) PPP₇₀-*b*-PT₇₀

(d) PPP₇₀-*b*-PT₉₀



	PPP ₇₀ - <i>b</i> -PT ₃₀	PPP ₇₀ - <i>b</i> -PT ₅₅	PPP70- <i>b</i> -PT70	PPP70- <i>b</i> -PT90
Height	4.4 nm	5.3 nm	6.4 nm	6.8 nm
Standard deviation	0.9 nm	0.6 nm	1.1 nm	0.8 nm

Figure S8. Height profiles of nanostructures from PPP-b-PT



Figure S9. Stability of nanostructures from PPP-b-PTs toward high temperature and sonication

(a) PPP₇₀-*b*-PT₃₀ : DLS profiles and UV-vis spectra with heat treatment up to 80 °C



(b) PPP₇₀-*b*-PT₅₅ : DLS profiles and UV-vis spectra with heat treatment up to 80 °C



(c) PPP_{70} -*b*- PT_{70} : AFM images are obtained (1) after sonication for 15 min and for 240 min at 25-40 °C. or (2) after spincoating of heated solution on HOPG. (3) UV-vis spectra with heat treatment up to 80 °C



(d) PPP_{70} -*b*- PT_{90} : AFM images are obtained after (1) sonication for 8 min and for 240 min at 25-40 °C, or (2) after spincoating of heated solution on HOPG. (3) UV-vis spectra with heat treatment up to 80 °C







(e) PPP₇₀-*b*-PT₉₀



References

(S1) T. Vahlenkamp and G. Wegner, Macromol. Chem. Phys., 1994, 195, 1933.