Supporting Information for:

In-Situ Fabrication of Poly(3-hexylthiophene)/ZnO Hybrid Nanowires with D/A Parallel-Lane Structure and Their Application in Photovoltaic Devices

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Experimental Section

Materials: All synthetic reactions were carried out under purified nitrogen. Before use, tetrahydrofuran (THF) and toluene were dried over sodium metal and freshly distilled. Additionally, 3-bromothiophene, 1-bromohexane, magnesium, *N*-bromosuccinimide (NBS), isopropylmagnesium chloride, [1,3-bis(diphenylphosphino) propane] dichloronickel (II) ($Ni(dppp)Cl_2$), and zinc acetate dehydrate were used as received without further purification.

Synthesis of P3HT Homopolymer: First, 2,5-dibromo-3-hexylthiophene monomer was synthesized by following literature procedures.[1, 2] Subsequently, the synthesized monomers were added into a pre-dried round-bottom flask which was then evacuated under reduced pressure to remove water and oxygen. Dried THF were then added into the flask, and the solution was stirred under dry nitrogen. After a complete mixing, isopropylmagnesium chloride was added via syringe and the resulting mixture was refluxed at 70°C for 2hrs. Then, the solution was cooled to room temperature, followed by adding [1,3-bis(diphenylphosphino) propane] dichloronickel (II) ($Ni(dppp)Cl_2$) into the flask. Upon stirring for polymerization for 2 hrs, the desired product was precipitated into methanol and washed by using Soxhlet apparatus with methanol and toluene sequentially. The residual solvent in P3HT was removed by drying it in a vacuum oven at 50°C for 3 days. The molecular weight and its distribution of the P3HT sample were measured by using a GPC (Waters 2695) equipped with two Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414) and a photodiode array absorbance detector (Waters 2996). THF was used as the mobile phase at a flow rate of 1mL/min. Figure S1 shows the GPC result of the synthesized P3HT sample (———). Based on the GPC data, it can be observed that the P3HT sample has a number-average molecular weight of 25300 g/mol and a polydispersity (PDI) of ~1.24.

Effect of Thermal Oxidation Treatment on P3HT: In this study, a brief thermal oxidation treatment (170°C for 30 min in air) was applied to P3HT/Zn^{2+} sample for the fabrication of in-situ synthesized P3HT/ZnO hybrid film. In order to examine whether this air annealing step might be chemically damaging P3HT, we additionally perform GPC measurements on P3HT before and after the heating step. As shown in Figure S1, the retention time and the shape of the GPC chromatograms of P3HT before (——) and after (– –) the heating step do not change significantly. Therefore, this annealing step does not induce significant chain-scission effect on P3HT.

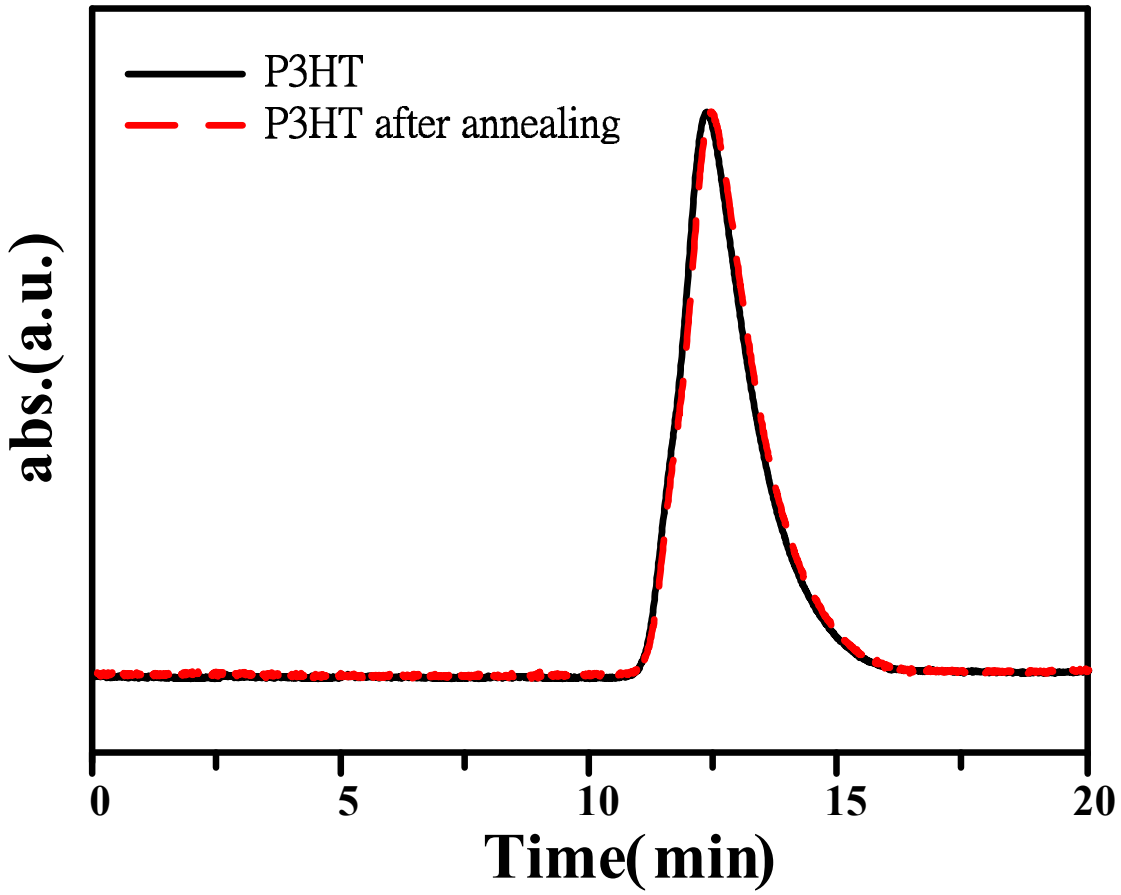

Figure S1. GPC trace of the P3HT homopolymer before (——) and after (– –) the air annealing process at 170°C for 30 min.

Table S1. J-V performance of the P3HT/ZnO photovoltaic devices.[a]

sample	Molar Ratio of P3HT : ZnO	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	series resistance (Ωcm^2)
P3HT/ex-situ ZnO blend	1:1	0.50±0.01	0.35±0.02	39.20±0.78	0.07±0.01	(1120±6)
P3HT/ZnO-A (embossed nanowires)	1:1	0.43±0.01	1.38±0.04	38.01±1.78	0.22±0.02	(93±3)
P3HT/ ZnO-B (parallel-lane nanowires)	1:1	0.44±0.01	3.47±0.11	39.99±2.01	0.61±0.06	(40±3)

[a] The photovoltaic values are averages and standard deviations of 4-5 individual cells.

References:

1. Lowe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999,** 11, 250-253.

2. Lowe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001,** 34, 4324-4333.