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Supporting Information

One-Step In Situ Hydrothermal Fabrication of D/A Poly(3-hexylthiophene)/TiO_2 Hybrid Nanowires and Its Application in Photovoltaic Devices

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Materials:

Cholorobenzene (CB) and tetrahydrofuran (THF) were dried over sodium metal and freshly distilled before use. Isopropylmagnesium chloride (*i*-PrMgCl, 2.0 M in THF), [1,3-bis(diphenylphosphino)propane]dichloronickel (II) (Ni(dppp)Cl_2), and titanium (IV) tetraisopropoxide (TTIP) were purchased from Aldrich Chemical and used as received without further purification. Without additional notes, all other reagents and solvents were commercially available and used directly without further purification. All synthetic reactions were carried out under purified nitrogen. High purity nitrogen was purchased (99.995% pure) and further purified by passing it through a column of molecular sieves and a BTS (Fluka) catalytic oxygen trap.

Synthesis of P3HT Homopolymer:

At first, 2,5-dibromo-3-hexylthiophene monomer was synthesized by slightly modified method from the previous literature procedure.[1-3] Subsequently, the P3HT polymerization was prepared by following literature procedures.[4-6] All glass apparatuses were dried prior to use. The synthesized monomers were added into a round-bottomed flask equipped with a high vacuum Rotaflo stopcock, which was then evacuated under reduced pressure to remove water and oxygen. Freshly distilled THF were then added into the flask via a double-tipped stainless steel needle under the protection of nitrogen, and the solution was mixed with a magnetic stirrer under dry nitrogen. After a complete mixing, *i*-PrMgCl was added via syringe and the resulting mixture was refluxed at 70 °C for 2 hr. Then, the solution was cooled to room temperature, followed by adding a suspension of Ni(dppp)Cl_2 in THF into the flask via a syringe. Upon stirring for polymerization for 2 hr, the reaction was quenched by pouring of HCl (aq., 30 wt%) into the mixture. The polymer mixture was extracted with $CHCl_3$ and dried over anhydrous $MgSO_4$. The crude product was precipitated in methanol and washed by using Soxhlet apparatus with methanol, hexane and chloroform sequentially. The residual solvent was removed by evaporation to give a solid product and then stored under nitrogen atmosphere.

Gel Permeation Chromatography (GPC)

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 1 mL/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 *Mn* of 56,200 g/mol and a polydispersity (PDI) of ~1.48.

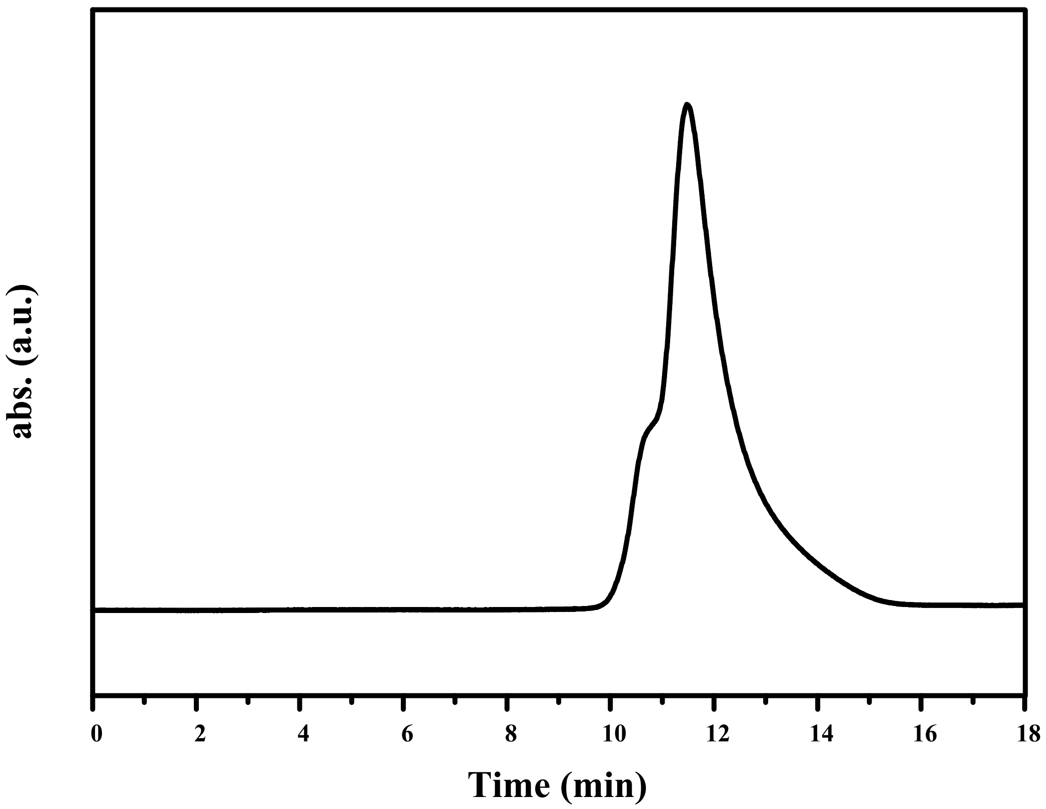

Figure S1. GPC trace of the P3HT56 homopolymer synthesized by using the Grignard metathesis method.

Table S1. Performance of P3HT/TiO_2 hybrid photovoltaic devices.[a]

Sample	Ratio of P3HT:TiO_2	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE_{best} (%)
P3HT/ex-situ TiO_2 blend	1:1	0.488 ± 0.013	0.164 ± 0.036	36.81 ± 4.64	0.03
in situ P3HT/TiO_2 hybrid	1:1	0.574 ± 0.023	0.412 ± 0.046	48.94 ± 4.29	0.14
in situ P3HT/TiO_2 hybrid	1:2	0.430 ± 0.014	0.552 ± 0.034	39.87 ± 3.08	0.11

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

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