Supporting Information for:

In-situ Growth of Rodlike ZnO Nanocrystals Assembled by Nanoparticles in Self-assembling Diblock Copolymer for Heterojunction Optoelectronics

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Experimental

Materials. All reactions were conducted under prepurified nitrogen, using oven-dried glassware. All solvents were freshly distilled prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium and calcium hydride (CaH₂) respectively.

Structural analysis of synthesized polymers was performed by using FT-IR and ¹H NMR spectroscopy. ¹H NMR spectra were recorded on a 600 MHz Varian spectrometer, using deuterated chloroform as a solvent. TMS was used as reference. Molecular weight of the polymers was determined by gel permeation chromatography (GPC). The gel permeation chromatography (GPC), so-called size-exclusion chromatography (SEC) analysis, was conducted with a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm×300 mm, 10³-10⁴Å) to separate molecular weight (MW) ranging from 10² to 10⁶.

Synthesis of vinyl terminated P3HT (P3HT- vinyl)

A dry 250 mL three-neck flask was flushed with N₂ and was charged with 2,5-dibromo-3-hexylthiophene (9.8 g, 30 mmol) and anhydrous THF (150 mL). A 2 M solution of butyl magnesium chloride (15 mL, 30 mmol) in diethyl ether (Et₂O) was added via a syringe, and the reaction mixture was gently refluxed for 90 min. The reaction mixture was allowed to cool down to room temperature, at which time Ni(dpdp)Cl₂ (0.3 g, 0.55 mmol) was added to the reaction mixture. The polymerization was allowed to proceed for 15 min at room temperature followed by the addition of a 1 M solution of vinyl magnesium bromide (6 mL, 6 mmol). The reaction mixture was stirred for 5 min followed by quenching in methanol. The polymer was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by ¹H NMR. Molecular weight of the polymers was determined by gel permeation chromatography (GPC) Mw = 22000.
\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): $\delta$H 6.98 \, (s, 1H), 6.61 \, (t, 1H), 5.52 \, (d, 2H), 5.13 \, (d, 2H), 2.80 \, (t, 2H), 1.66 \, (t, 2H), 1.35-1.41 \, (m, 6H), 0.91 \, (t, 3H).

**Synthesis of hydroxy terminated P3HT (P3HT-OH)**

Vinyl terminated P3HT (2.2 g, 0.1 mmol) was dissolved in anhydrous THF (25 mL) under N\textsubscript{2}. To this reaction mixture, a 0.5 M solution of 9-BBN (2 mL, 1 mmol) in anhydrous THF was added via a syringe. The reaction mixture was stirred for 24 h at 40\textdegree C, at which point a 6 M solution of NaOH (1 mL) was added to the reaction flask. The reaction mixture was stirred for another 15 min (at which point the oil bath was removed). The reaction mixture was allowed to cool down to RT followed by addition of a 33\% aqueous solution of hydrogen peroxide (1 mL), and the reaction was allowed to proceed for additional 24 h at 40\textdegree C. The P3HT-OH was isolated by precipitation in a methanol–water mixture.

The conversion of vinyl to P3HT-OH was indicated by the complete disappearance of vinyl protons and the appearance of new signals at 3.9 ppm (t) due to the methylene protons.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): $\delta$H 6.98 \, (s, 1H), 3.72 \, (t, 2H), 3.21 \, (t, 2H), 2.69 \, (t, 2H), 1.62 \, (t, 2H), 1.35-1.43 \, (m, 6H), 0.91 \, (d, 3H).

**Synthesis of bromoester terminated poly(3-hexylthiophene) macroinitiator (P3HT-Br)**

P3HT-OH (2.2 g, 0.1 mmol) was dissolved in anhydrous THF (25 mL) under N\textsubscript{2}. The reaction mixture was stirred for 15 min at 40\textdegree C followed by addition of triethylamine (9 mL, 66 mmol) and a drop-wise addition of 2-bromoisobutyrate bromide (7.5 mL, 60 mmol). The reaction mixture was stirred for 24 h at 40\textdegree C. The resulting P3HT-Br macroinitiator was precipitated in methanol. Formation of P3HT-Br was also confirmed by $\textsuperscript{1}$HNMR.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): $\delta$H 6.98 \, (s, 1H), 4.22 \, (t, 2H), 3.19 \, (s, 6H), 3.15 \, (t, 2H), 1.70 \, (s, 6H), 1.35-1.41 \, (m, 6H), 0.91 \, (t, 3H).
Figure S1. TEM image of P3HT-b-PZnMAAc assembly
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**Figure S2.** EDS spectrum of rodlike ZnO nanocrystals