

**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 (CaH<sub>2</sub>) respectively.

**Structural analysis** of synthesized polymers was performed by using FT-IR and <sup>1</sup>HNMR spectroscopy. <sup>1</sup>HNMR 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, 10<sup>3</sup>-10<sup>4</sup>Å) to separate molecular weight (MW) ranging from 10<sup>2</sup> to 10<sup>6</sup>.

### Synthesis of vinyl terminated P3HT (P3HT- vinyl)

A dry 250 mL three-neck flask was flushed with N<sub>2</sub> 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 (Et<sub>2</sub>O) 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(dppp)Cl<sub>2</sub> (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 <sup>1</sup>H NMR. Molecular weight of the polymers was determined by gel permeation chromatography (GPC) Mw = 22000.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  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  $\text{N}_2$ . 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  $40^\circ\text{C}$ , 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  $40^\circ\text{C}$ . The **P3HT-OH** was isolated by precipitation in a methanol–water mixture.

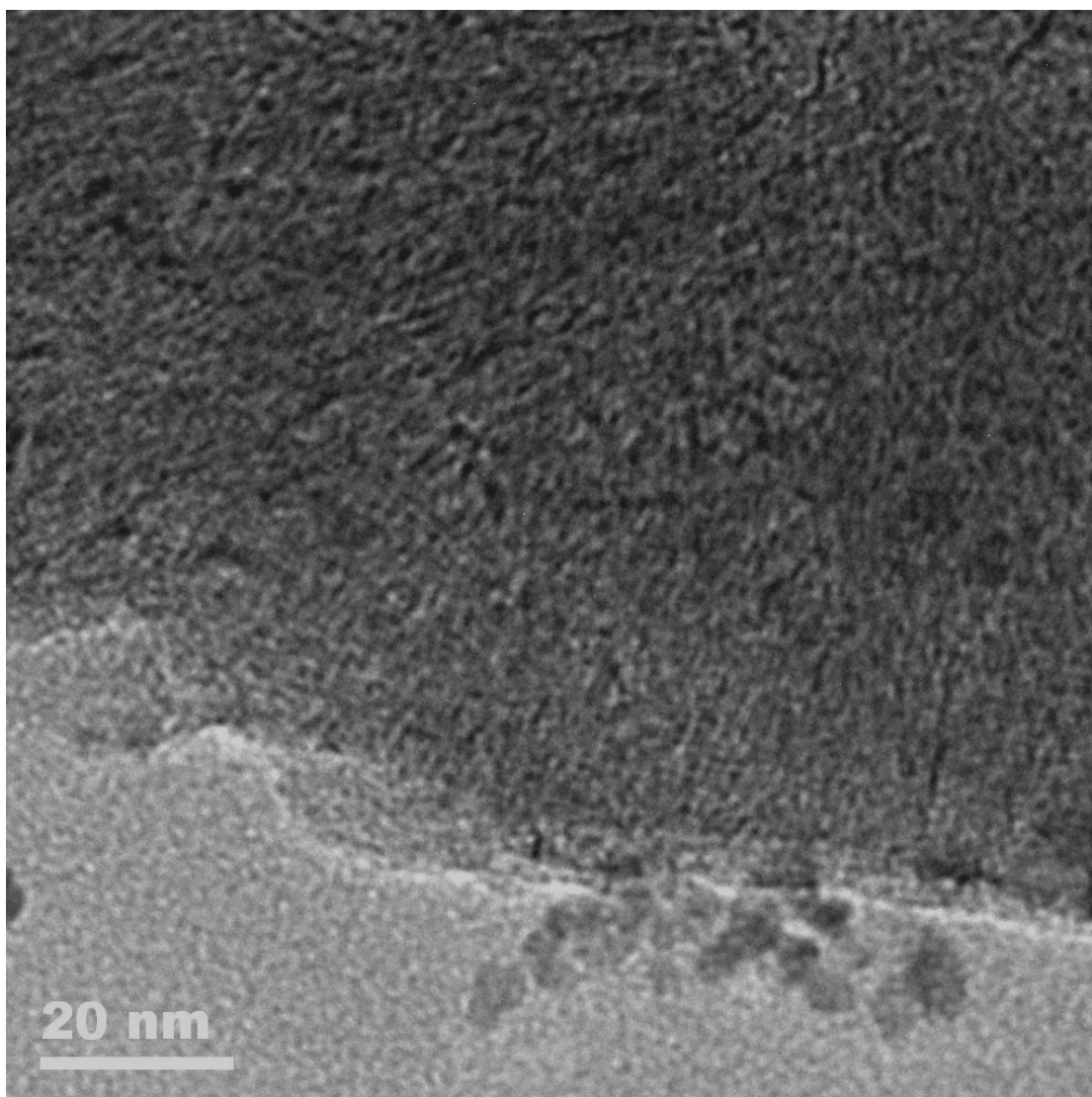
The conversion of vinyl to **P3HT-OH** was indicated by the complete disappearance of vinyl protons and the appearance of new signals at 3.9 ppm (t) due to the methylene protons.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  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).

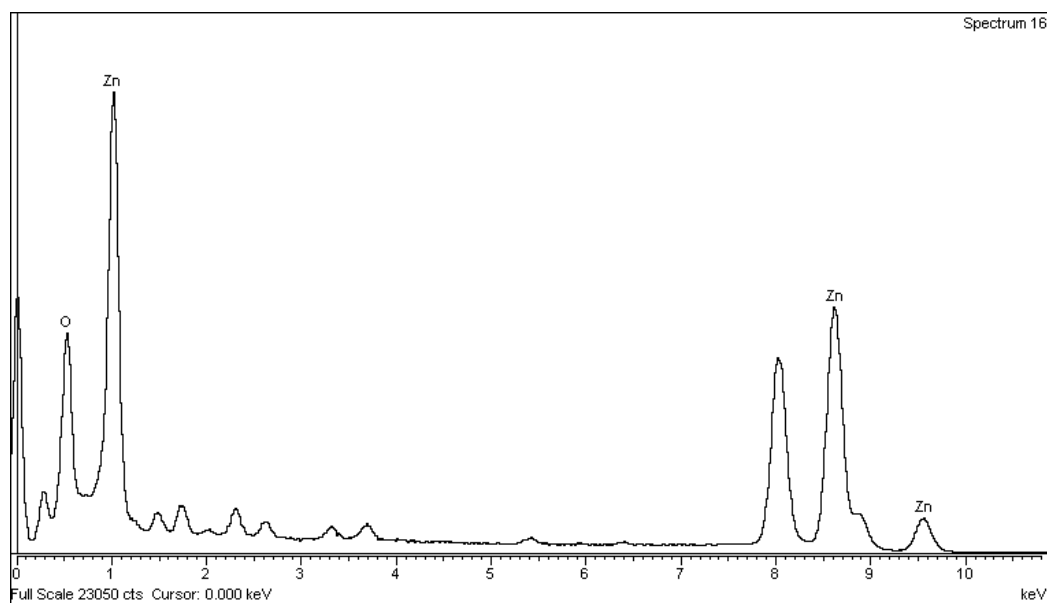
### Synthesis of bromoester terminated poly(3-hexylthiophene) macroinitiator (P3HT-Br)

**P3HT-OH** (2.2 g, 0.1 mmol) was dissolved in anhydrous THF (25 mL) under  $\text{N}_2$ . The reaction mixture was stirred for 15 min at  $40^\circ\text{C}$  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  $40^\circ\text{C}$ . The resulting **P3HT-Br** macroinitiator was precipitated in methanol. Formation of **P3HT-Br** was also confirmed by  $^1\text{H}$ NMR .

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  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



Element	Peak	Area	k	Abs	Weight	Weight	Atom
					%	%	c%
	Area	Sigma	factor	Corrn.		Sigma	
O K	81742	686	1.810	1.000	33.21	0.21	67.01
Zn K	20758	882	1.434	1.000	66.79	0.21	32.99
Totals					100.00		

**Figure S2.** EDS spectrum of rodlike ZnO nanocrystals