

Supporting Information for:

Understanding the Mechanism of Poly(3-hexylthiophene)-*b*-poly(4-vinylpyridine)

as a Nanostructuring Compatibilizer for Poly(3-hexylthiophene)/ZnO-based

Hybrid Solar Cells Performance Improvement

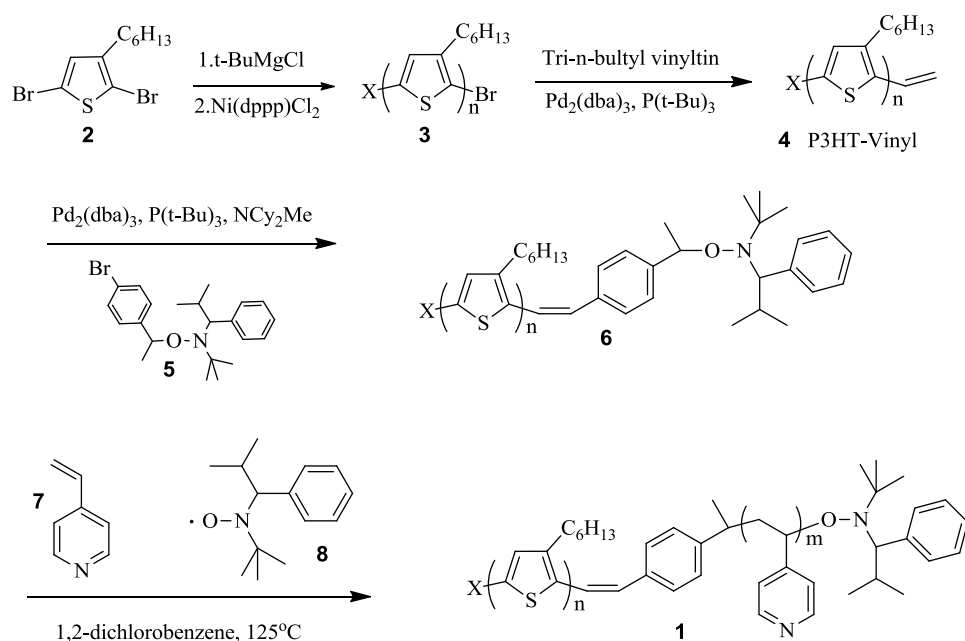
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Scheme S1. Schematic illustration of the preparation of **P3HT-*b*-P4VP**.

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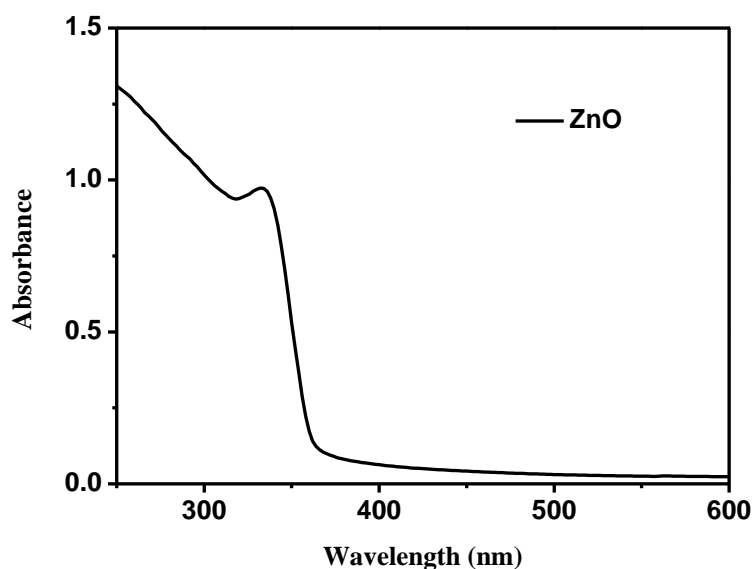


Figure S1 UV-vis absorption spectrum of ZnO NPs.

Experimental details

Synthesis of vinyl terminated P3HT (P3HT- vinyl) (4)

A dry 250 mL three-neck flask was flushed with N_2 and was charged with 2, 5-dibromo-3-hexylthiophene (4.9 g, 15 mmol) and anhydrous tetrahydrofuran (THF) (80 mL). A 2 M solution of butyl magnesium chloride (7.5 mL, 15 mmol) in diethyl ether (Et_2O) 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 $Ni(dppp)Cl_2$ (0.15 g, 0.28 mmol) was added to the reaction mixture. The polymerization was allowed to proceed for 6 hrs at room temperature followed by the addition of a 1 M solution of vinyl magnesium bromide (3 mL, 3 mmol). The reaction mixture was stirred for 30 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 polymer was determined by gel permeation chromatography (GPC), **Figure S3**, $M_w = 13000$.

^1H NMR (600 MHz, CDCl_3): δ_{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 P3HT alkoxyamine macroinitiator (P3HT-TIPNO) (6)

Under prepurified nitrogen flow, vinyl-terminated P3HT **4** (1.3 g, 0.1 mmol) was dissolved in anhydrous THF (80 mL) in a Schlenk flask. To this was added $\text{Pd}_2(\text{dba})_3$ (36 mg), tri(*t*-butyl)phosphine (30 mg), methyl dicyclohexane amine (1.8 g) and phenylbromide-alkoxyamine **5**. The reaction mixture was stirred at 55 °C for 24 hrs. The polymer precipitated repeatedly into methanol, and dried under vacuum to give the desired P3HT macroinitiator **6**.

^1H NMR (600 MHz, CDCl_3): δ_{H} 7.6-7.4 (br), 7.4-7.2 (br), 6.98 (s), 4.9 (br), 3.51 (d), 3.31 (d), 2.80 (t), 1.75-1.30 (br), 1.10 (s), 0.91 (t), 0.82 (s), 0.61 (d), 0.26 (d).

Synthesis of poly(3-hexylthiophene)-*b*-poly(4-vinylpyridine) (P3HT-*b*-P4VP) (1)

To a dry Schlenk tube P3HT-macroinitiator **6** (0.52g, 0.04mmol), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl **5** dissolved in 20 mL distilled *o*-dichlorobenzene (*o*-DCB) and 8 mL distilled 4-vinylpyridine was added flooded with argon. The reaction mixture was degassed with three freeze, pump, thaw cycles and the polymerization was started by placing the Schlenk tube in a 125 °C hot oil bath. After 3h the Schlenk tube was poured into liquid nitrogen in order to quench the

polymerization. The raw polymer mixture was diluted with chloroform and precipitated in pentane. The polymer was filtered and washed with hydrochloric acid to protonate the P4VP block. The pure polymer was obtained by dissolution in chloroform, precipitation in pentane, filtration and drying under vacuum.

^1H NMR (600 MHz, CDCl_3): 8.58-8.05 (m, 2H, P4VP), 6.98 (s, H, P3HT), 6.72-6.11 (m, 2H, P4VP), 2.80 (t, 2H, $-\text{CH}_2$, P3HT), 1.82-1.60 (m, 2H, $-\text{CH}_2$, P3HT), 1.50-1.10 (m, 6 H, P3HT and m, 2H, CH_2 , P4VP), 0.98-0.76 (m, 3H, CH_3);

The molecular weight of P3HT-*b*-P4VP was $M_w = 17000$ with a polydispersity index (PDI) of 1.32 determined by a tetrahydrofuran determined by gel permeation chromatography (GPC), **Figure S3**, (P3HT block $M_w = 13000$, and P4VP block $M_w = 4000$).

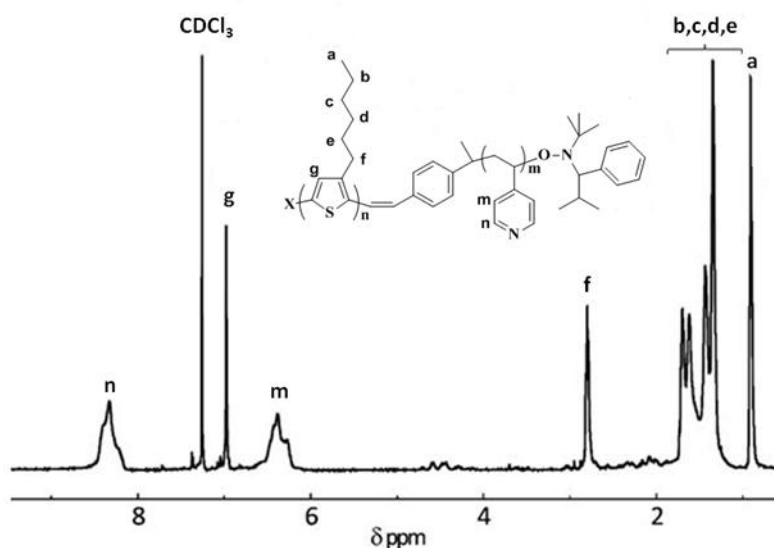


Figure S2. ^1H NMR spectrum of P3HT-*b*-P4VP diblock copolymer.

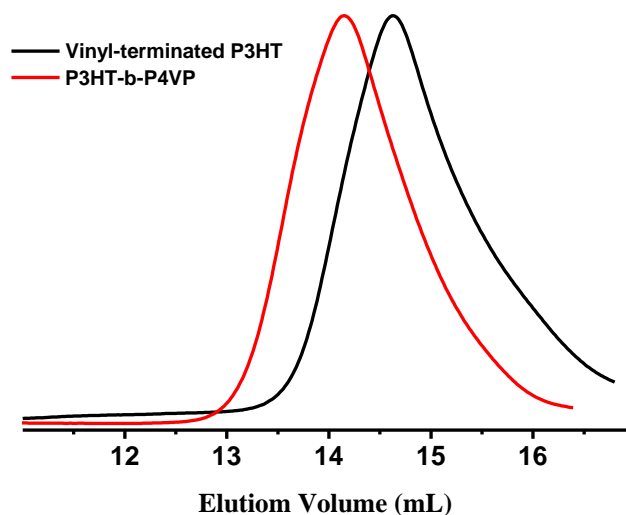
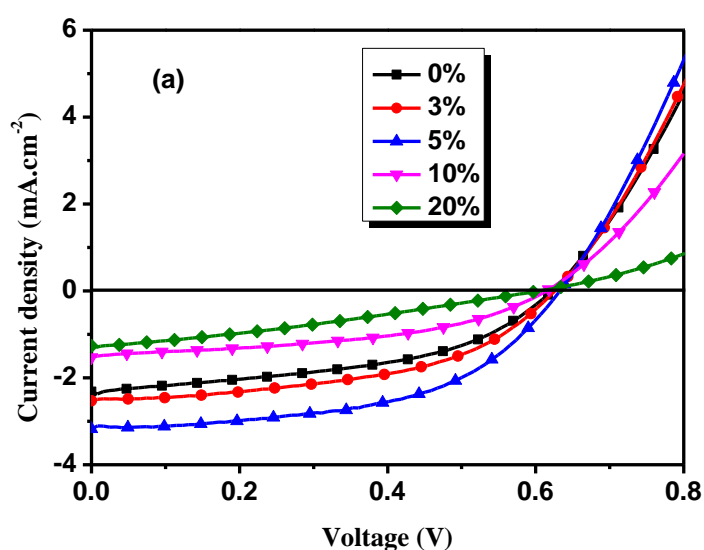


Figure S3. GPC profile of vinyl-terminated P3HT **4** and **P3HT-*b*-P4VP** diblock copolymer.

In order to get insight into the photophysical properties of the P3HT-*b*-P4VP containing films, UV-vis absorption spectra have been performed on films coated on quartz substrates, prepared following the same methodology as for the active layers of the devices. In **Figure S6**, normalized UV-vis absorption spectra are shown as a function of wavelength for pristine P3HT, and P3HT/ZnO blend at different P3HT-*b*-P4VP weight fractions. The spectrum of the P3HT/ZnO films at different P3HT-*b*-P4VP weight fractions are dominated by the long wavelength aggregate absorption, with clear A_{0-1} and A_{0-0} (where subscripts denote respective vibronic transitions) peaks at 2.214 eV (560 nm) and 2.034 eV (610 nm), respectively. The shoulders due to vibronic transitions in the UV-vis spectra of the P3HT/ZnO films are enhanced, especially when the P3HT-*b*-P4VP weight fractions is 5%, as interpreted by

the increased shoulders at 2.214 eV (560 nm) and 2.034 eV (610 nm). The presence of these shoulders correlates to enhanced hole mobility in the polymer.¹⁻³ Appearance of red-shift in P3HT/ZnO at different P3HT-b-P4VP weight fractions are observed compared to pristine P3HT. The appearance of red shifted species is usually assigned to the formation of crystallites and an indication for more ordered structures.⁴ Generally, a higher degree of P3HT crystallinity can be represented by a relatively large red-shift of the spectrum in the wavelength range of P3HT absorption, because of an increase of effective conjugations, and by clearer vibronic shoulders at the longer-wavelength side of an absorption maximum due to an enhanced interchain interaction.⁵



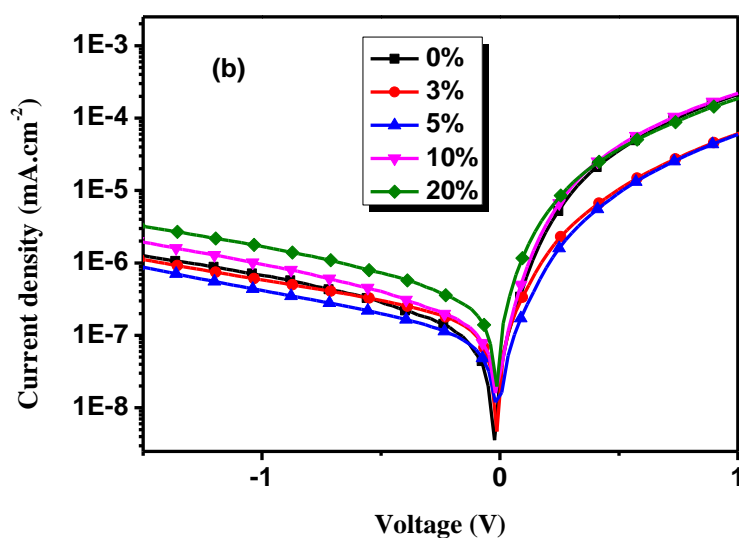


Figure S4. (a) Current density-voltage characteristics and (b) dark current density versus bias voltage of P3HT/ZnO hybrid solar cells at different P3HT-b-P4VP weight fractions.

Table S1. Photovoltaic characteristics of P3HT/ZnO-based BHJ solar cells with different ratios of P3HT-b-P4VP diblock copolymer.

P3HT-b-P4VP weight ratio (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0	2.32	0.621	46.7	0.67
3	2.53	0.625	49.4	0.78
5	3.18	0.632	52.4	1.05
10	1.53	0.613	44.4	0.42
20	1.27	0.602	30.5	0.23

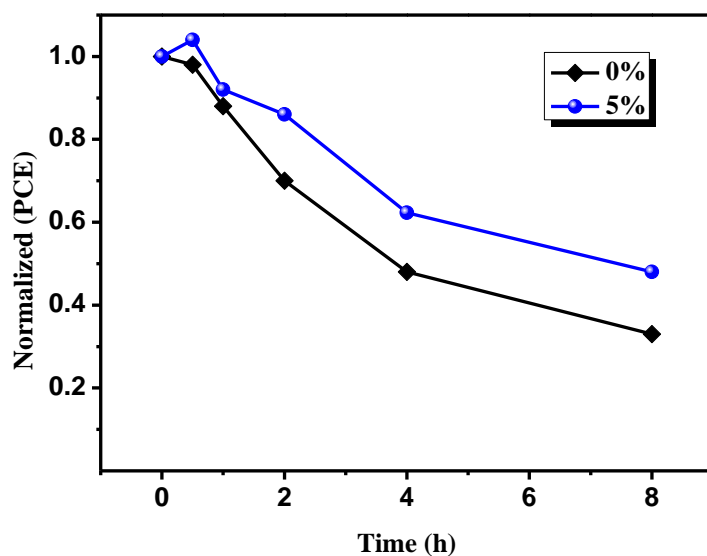


Figure S5. Normalized power conversion efficient (PCE) of photovoltaic cells during thermal annealing at 120 °C. The efficiency of each device was normalized to its initial efficiency.

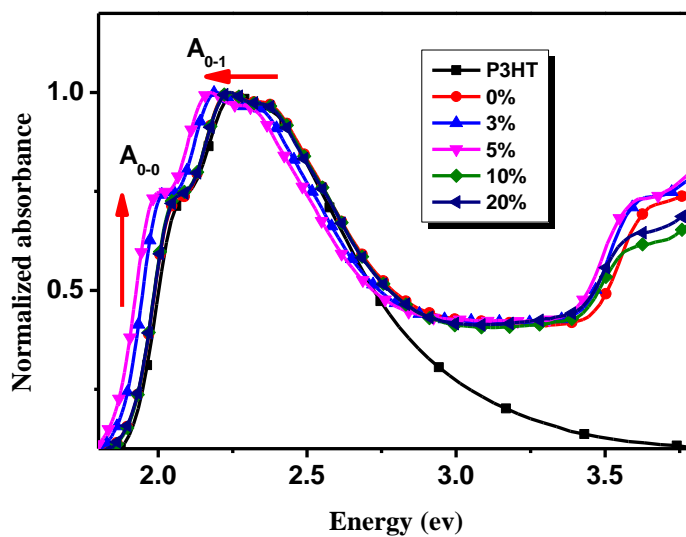
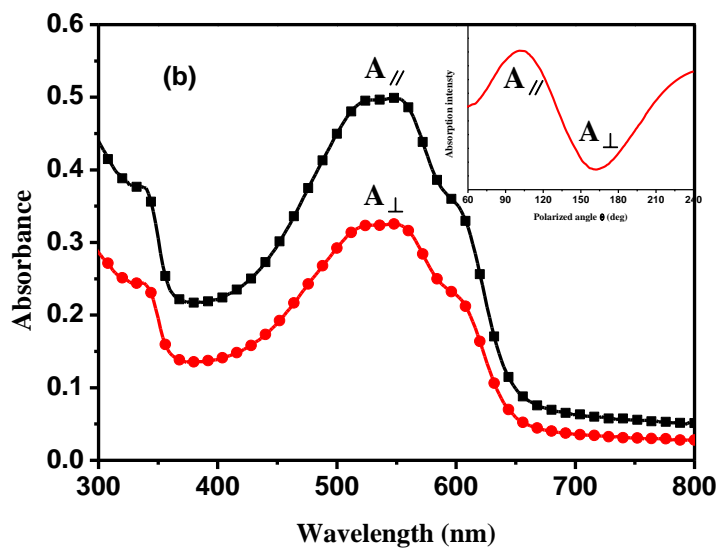
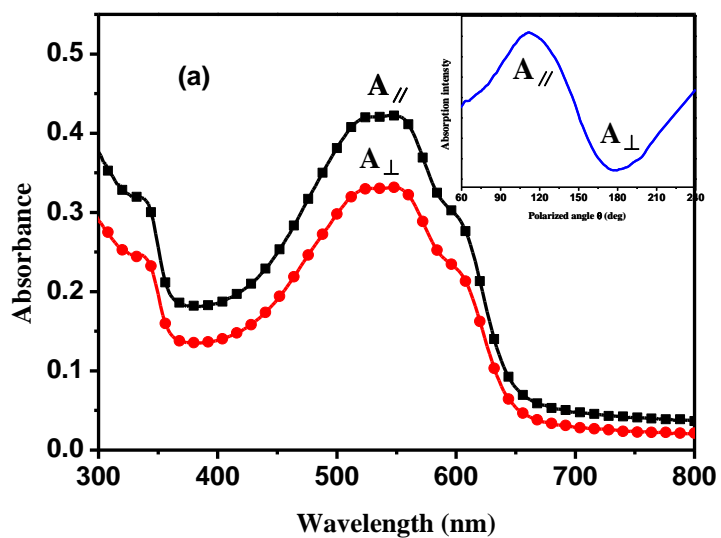


Figure S6. Normalized ultraviolet–visible absorption spectra for pristine P3HT and P3HT/ZnO blend at different P3HT-b-P4VP weight fractions.



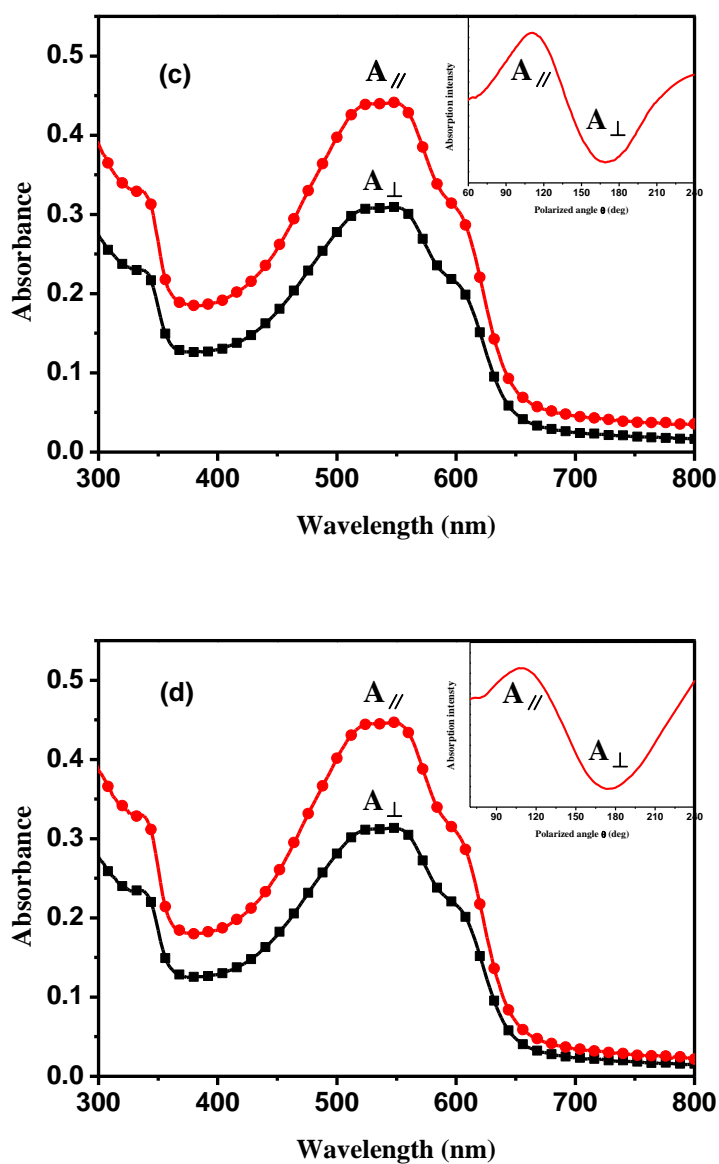
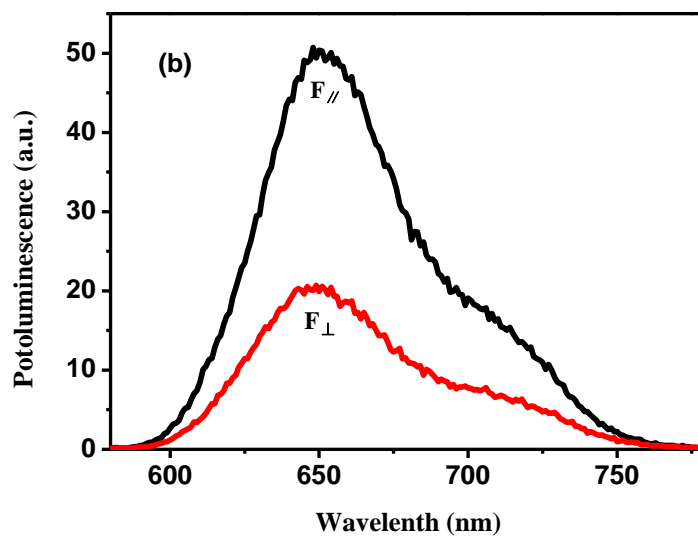
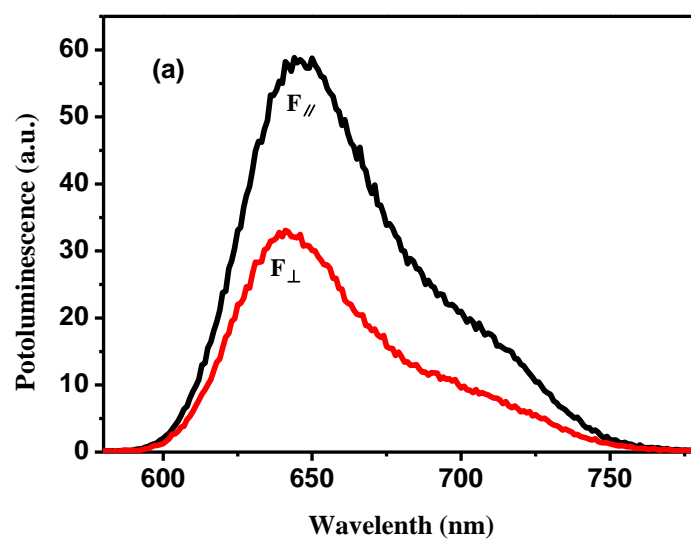
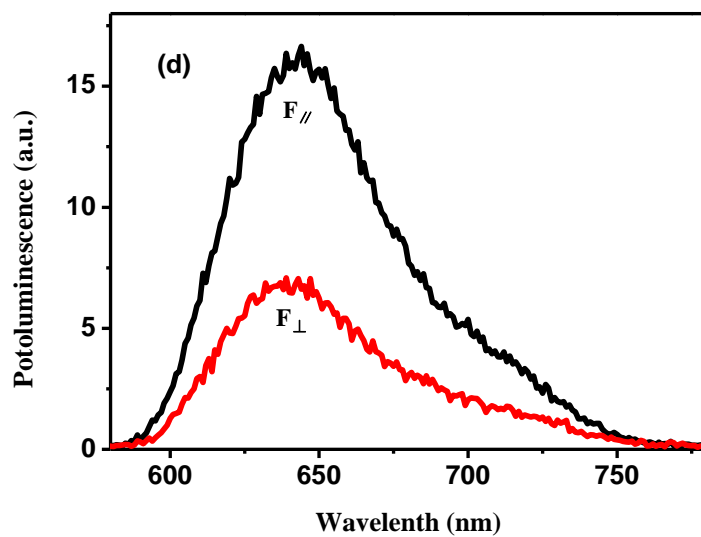
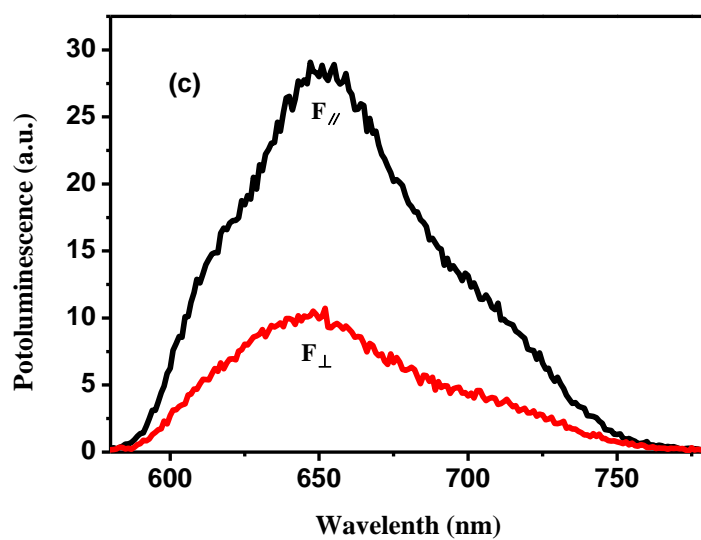


Figure S7. Polarized absorbance spectra of P3HT/ZnO blend films at different P3HT-b-P4VP weight fractions (a) 0%, (b) 3% , (c) 10% and (d) 20%. $A_{//}$ and A_{\perp} are the absorbances measured with the light polarized parallel and perpendicular to the P3HT molecule, respectively. The inset shows the polarized absorption for film at 560 nm.





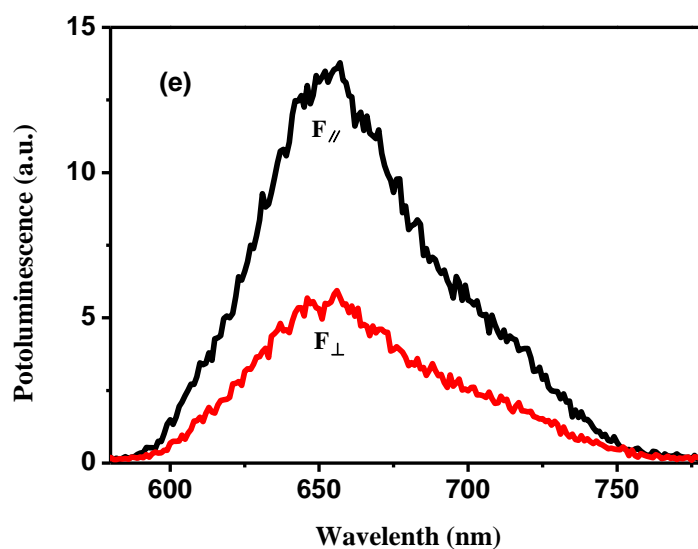


Figure S8. Polarized photoluminescence spectra of P3HT/ZnO blend films at different P3HT-b-P4VP weight fractions (a) 0%, (b) 3% , (c) 5%, (d) 10% and (e) 20%. $F_{//}$ and F_{\perp} are the fluorescence intensities in the direction parallel and perpendicular to the P3HT molecule.

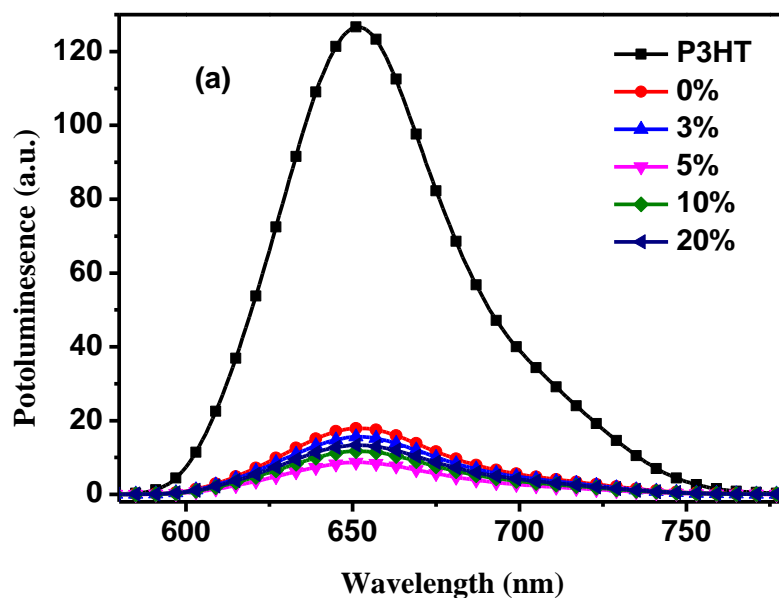


Figure S9. Fluorescence spectra for pristine P3HT and P3HT/ZnO blend at different P3HT-b-P4VP weight fractions. (monitored at $\lambda_{exc} = 460$ nm).

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