

Supplementary Information

Polymer-quantum dot composite hybrid solar cells with bi-continuous network morphology by using the block copolymer Poly(3-hexylthiophene)-b-polystyrene or its blend with Poly(3-hexylthiophene) as donor

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S1. Experimental Section

A. General Measurement and Characterization

B. Materials

C. Synthetic Methods

S2. FTIR, UV-Vis spectra of polymers

S3. Performance characteristics of quantum dots hybrid solar cell at different weight ratio and with different thermal annealing temperature

S1. Experimental Section

A. General Measurement and Characterization

The ^1H NMR was measured by using VARIAN UNITYINOVA 500 NMR. The thickness of solid film was measured by a Tencor P-10 Surface Profiler. UV-Vis absorption spectra are measured by Lambda 19 UV-Vis spectroscopy from Perkin-Elmer. Gel permeation chromatography (GPC) measurements were performed on a Waters separations module apparatus with Waters 2414 Refractive Index Detector and series columns of Styragel HR2 and Styragel HR 4E, THF as the eluent (flow rate 1 mL/min, 35 °C) and monodispersed polystyrenes as calibration standard. FTIR spectra were measured by Nicolet iS50 FTIR Spectrometer from Thermo Fisher Scientific. The conductivity of thin-film was measured by 4-point method with a Keithley 2400 ($I-V$) digital source meter.

B. Materials

The hole transport material PEDOT:PSS (Baytron PVP. AI-4083) with a conductivity of 2×10^{-4} - 2×10^{-3} S cm^{-1} was purchased from Heraeus. 2,5-Dibromo-3-hexylthiophene 97%, Oleic acid 90% (OA), 1-octadecene (ODE, 90%), Bis(trimethylsilyl)sulfide (TMS), 1,3-benzenedithiol (BDT), Tetrakis(triphenylphosphine)palladium (0) 99% ($\text{Pd}(\text{PPh}_3)_4$), Anhydrous tetrahydrofuran >99.9% inhibitor-free, n-Octane anhydrous >99% were purchased from Sigma Aldrich. Styrene 99%, Lead (II) acetate trihydrate 99%, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 94% were purchased from Alfa Aesar. n-Butyllithium in n-Hexane (2.6 mol/L) was purchased from Kanto Chemical Co. [1,3-Bis(diphenylphosphino)propane]nikel(II)chloride 99% ($\text{Ni}(\text{dppp})\text{Cl}_2$) was purchased from Acros Organics. Chloroform 95%~100% containing 1% of Ethanol, Acetonitrile 95%, n-Hexane 95% were purchased from J.T. Baker.

C. Synthetic Methods

P3HT-Br: Regioregular poly(3-hexylthiophene) with bromo group at a terminal (P3HT-Br) were prepared in nitrogen atmosphere by the modified method previously reported. ^[S1, S2] A dry 50 mL three-neck round-bottom flask was charged with 2,5-dibromo-3-hexylthiophene (1.0 g, 3 mmol), and anhydrous THF (10 mL). A 2 M solution of tert-butylmagnesium chloride (1.5 mL, 3 mmol) in diethyl ether (Et₂O) was added via a deoxygenated syringe, and the reaction mixture was gently refluxed for 2 h. After the consumption of 2,5-dibromo-3-hexylthiophene the reaction mixture was cooled at 20-22 °C. Ni(dppp)Cl₂ (0.05 g, 0.06 mmol) was added as a suspension in 1 mL of anhydrous THF. The polymerization continued for 30 minutes and the mixture was poured into methanol to precipitate the product, then which was extracted by Soxhlet with methanol, acetone, hexane and THF to collect P3HT. P3HT dissolved in THF was characterized and used for the remaining experiments. Mn: 9,700 Dalton; Yield: 233 mg (23.3%).

PS-B(OR)₂: A dry 50 mL three-neck round-bottom flask with a stopcock was charged with anhydrous THF (20 mL) and cooled down to -78 °C. n-butyllithium (2.6 mol/L solution, 0.74 mL, 1.92 mmol) were successively added into the flask, and then 0.82 mL styrene monomer was slowly injected into the flask at -78 °C. After stirring for 5 min, 0.45 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was injected into the reaction mixture and then the temperature was increased up to room temperature under stirring and waiting for 2 hours. Finally, (PS-B(OR)₂) was collected by pouring into methanol. Mn: 7,340 Dalton; Yield: 659 mg (83.7%).

P3HT-b-PS: Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.023 g, 0.02 mmol), 3 M K₂CO₃ (aqueous solution, 1 ml), PS-B(OR)₂ (0.367 g, 0.05 mmol) and P3HT-Br (0.100 g, 0.0103 mmol), THF (5 mL) were placed into a flask equipped with a condenser, followed by freeze-and-thaw cycles to eliminate air in the mixture. Then the mixture was stirred for 120 h at 100 °C. The

product was reprecipitated in methanol and product then extracted by Soxhlet with methanol, acetone, hexane and THF was used to collect P3HT. Mn: 11,520 Dalton; Yield: 106 mg (89.33%).

PbS quantum dots: 1.52 g (4 mmol) PbAc.3H₂O, 3.0 mL OA and 20 mL ODE were mixed in a three-neck flask, which was dried to use under vacuum at 90°C overnight to remove residual water. Once the solution turned to clear, indicating a formation of lead oleate, the flask then heated to 100°C under nitrogen stream. 360 µL TMS in 10 mL ODE was rapidly injected into the lead oleate solution using syringe under nitrogen at 100°C. The solution changed to brown color immediately, indicating a formation of OA-capped PbS QDs. The QDs solution was removed from the heating mantle and then rapidly cooled down to room temperature by water bath. The QDs were precipitated by adding 100-200 mL acetone and centrifuged at 8000 rpm for 10 minutes under ambient condition. The supernatant was discarded and the resulting QDs were re-dispersed in hexane. The sediment was precipitated by acetone, centrifuged and re-dispersed in hexane. These purification steps were repeated for three times and the resulting QDs were re-dispersed in octane (25 mg/mL). The OA capped PbS QDs solution in octane were filtered through a 0.22 µm PTFE syringe filter and stored in nitrogen-filled glove box.

The size of quantum dot ($d = 3.09$ nm) was estimated by Iwan Moreels's equation:^[S3]

$$E_{gap} (eV) = 0.41 + [(0.0252d^2 + 0.283d)]^{-1}$$

where E_{gap} is a energy gap between HOMO and LUMO level which were calculated from UV-Vis absorption spectra (**Figure S1**) with the absorption peak at 950 (nm), $E_{gap} (eV) = [1243/(\text{wavelength})(\text{nm})]$, and d is diameter of QDs.

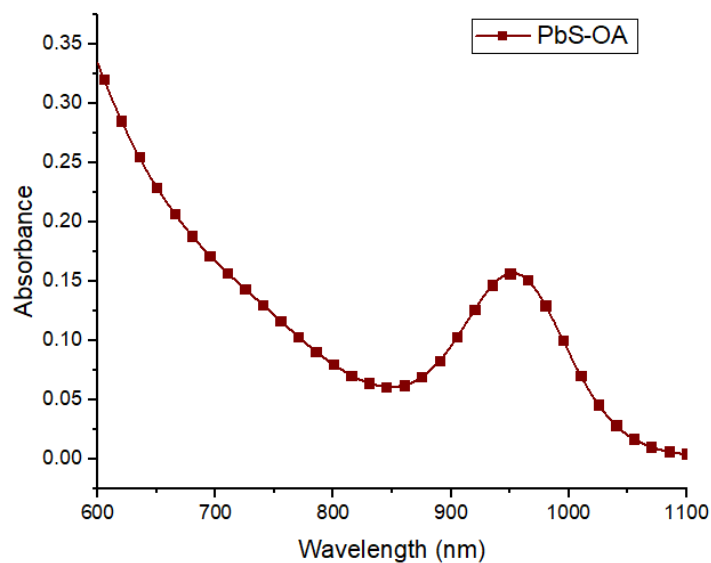


Figure S1: UV-Vis absorption spectra of PbS QDs in hexane.

S2. FTIR, UV-Vis spectra of polymers

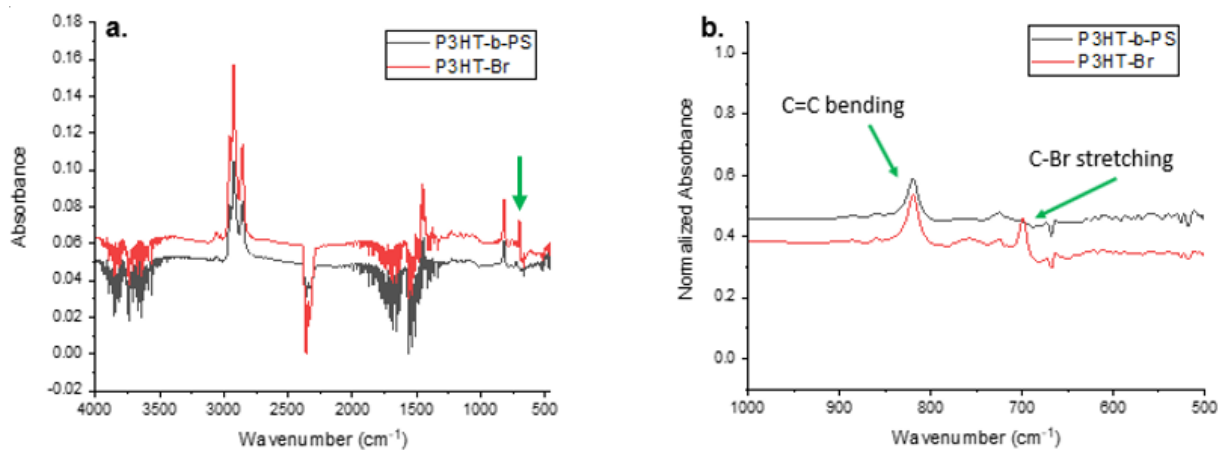


Figure S2: **a.** FTIR spectra of P3HT-b-PS and P3HT-Br, **b.** Magnification of FTIR spectrum from 500 (cm^{-1}) to 1000 (cm^{-1}).

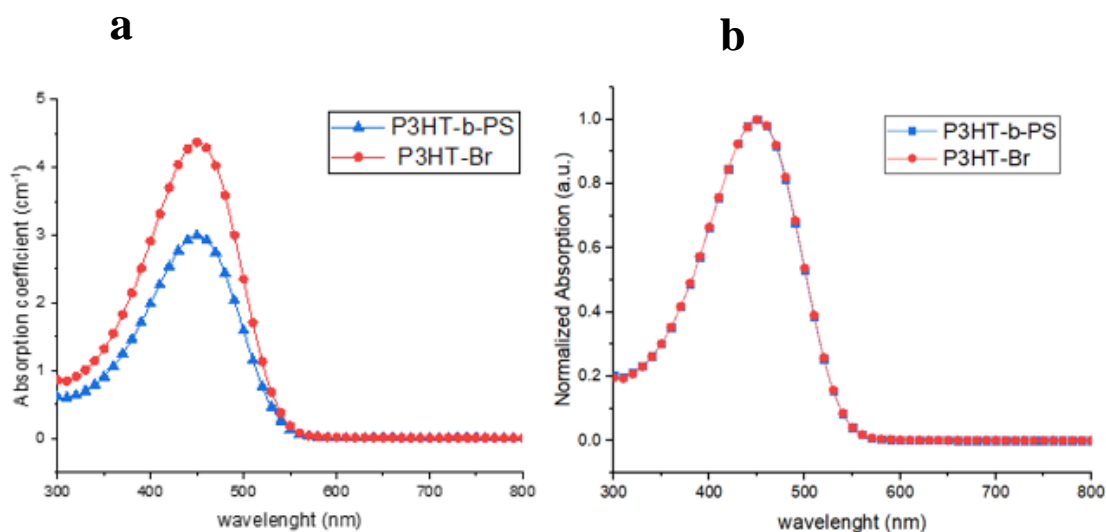


Figure S3: UV-Vis absorption spectra of P3HT-Br and P3HT-b-PS in chloroform at the concentration (1 mg/mL). **(a)** The absorption spectra based on absorption coefficient. **(b)** The normalized absorption spectra.

S3. Performance characteristics of quantum dots hybrid solar cell at different weight ratio and with different thermal annealing temperature

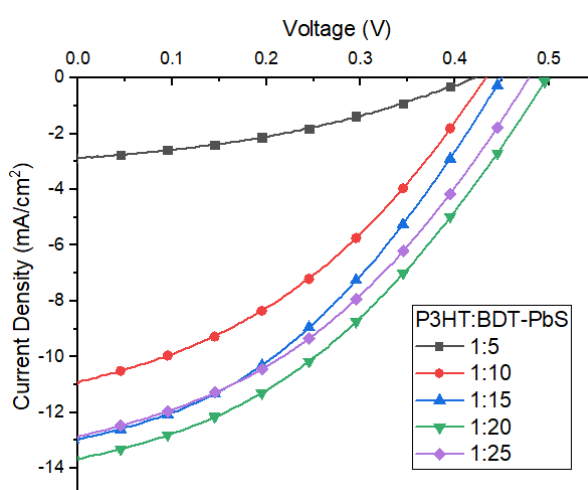


Figure S4: The current density-voltage of P3HT:BDT-PbS devices with various weight ratios

Table S1: The device performance of PbS QD hybrid solar cells^{a)} by using P3HT:PbS QD at various weight ratios and without thermal annealing.

P3HT:PbS (Weight ratio)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	R _{SH} (Ω·cm ²)	R _S (Ω·cm ²)
1:5	0.42	2.88	36.9	0.45	334.92	84.28
1:10	0.43	10.95	37.4	1.77	100.55	21.87
1:15	0.45	12.96	37.9	2.21	113.47	19.98
1:20	0.50	13.68	38.0	2.58	122.10	19.31
1.25	0.48	12.86	38.2	2.35	118.99	20.31

^{a)} The device configuration is ITO/PEDOT:PSS (40 nm)/P3HT:BDT-PbS (120 nm)/BDT-PbS (30 nm)/LiF (0.6 nm)/Al(100 nm).

b) With thermal annealing treatment at 175°C

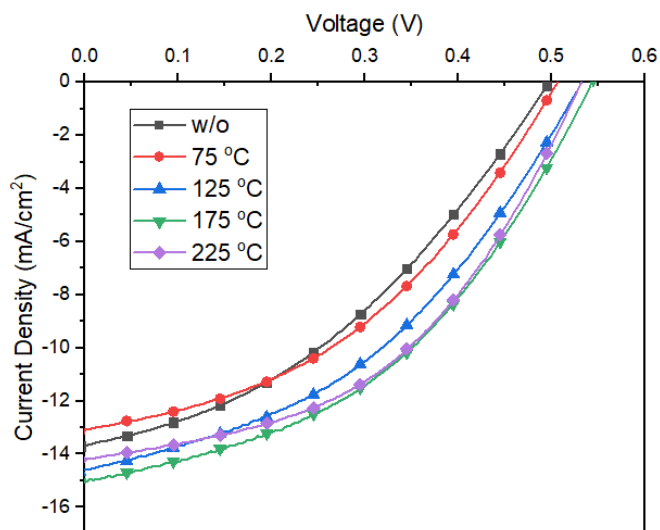


Figure S5: The current density-voltage of P3HT:BDT-PbS devices at 1:20 weight ratios and different thermal annealing temperature.

Table S2: The device performance of P3HT:PbS QD hybrid solar cell^{a)} at 1:20 weight ratio and different annealing temperatures.

Annealing temperature	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)	R _{SH} (Ω·cm ²)	R _S (Ω·cm ²)
w/o	0.50	13.68	38.0	2.58	122.10	19.31
75 °C	0.51	13.09	41.1	2.73	122.38	17.72
125 °C	0.53	14.58	41.1	3.19	121.99	16.70
175 °C	0.54	15.07	42.9	3.52	144.54	15.14
225 °C	0.53	14.16	46.2	3.45	200.14	15.47

^{a)} The device structure is ITO/PEDOT:PSS(40 nm)/P3HT:BDT-PbS(120nm)/BDT-PbS(30nm)LiF(0.6 nm)/Al(100 nm).

References

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