Electronic Supplementary Information (ESI)

High-Efficiency Perovskite Quantum Dot Solar Cells Benefiting from a Conjugated Polymer-Quantum Dot Bulk Heterojunction Connecting Layer

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1. Materials

Formamidine acetate (FAOAc, 99%, Aldrich), cesium carbonate (Cs_2CO_3, 99.9% purity, Sigma), lead iodine (PbI_2, 99.9% purity, Sigma), 1-octandecene (ODE, 90% purity, J&K), oleic acid (OA, 90% purity, Alfa), oleylamine (OAm, 90% purity, Alfa), n-hexane (97.5% purity, J&K), n-octane (anhydrous, ≥ 98% purity, Alfa), chloroform (CF, AR, Chinasun Specialty Products Co.,Ltd.), methyl acetate (MeOAc, anhydrous, 99.5% purity, Sigma), ethyl acetate (EtOAc, anhydrous, 99.8% purity, Sigma), toluene (98% purity, Chinasun Specialty Products Co., Ltd.), titanium tetrachloride ($TiCl_4$, ≥ 98% purity, Sinopharm Chemical Reagent Co.,Ltd.), tris(pentafluorophenyl)borane (95% purity, Acros Organics), poly(triarylamine) (PTAA) are purchased from Xi'an Polymer Light Technology Corp. (China). PTB7, PBDB-T, PCE-10 was purchased from 1-Materials and PTP8 was synthesized according to our previous reported work.[1] All the above materials were employed without further purification.

2. Synthesis of $CsPbI_3$ and $FAPbI_3$ QDs

For the synthesis of Cs-oleate: 0.5 g of Cs_2CO_3 powder, 2 mL of OA and 50 mL of ODE were mixed in a 100 mL three-neck flask, stirring at 90 ^oC for 60 min under vacuum to prepare Cs-oleate. Then, the flask was filled with N_2 and heated up to 120 ℃ until OA and Cs_2CO_3 fully reacted to form Cs-oleate. The Cs-oleate was stored at N_2 atmosphere and kept at 70 ^oC for QDs synthesis.

For the synthesis of FA-oleate: 2.605 g of FA-acetate powder and 50 mL of OA were added into a 100 mL three-neck flask and stirred under vacuum at 50 ^oC for one hour to synthesize FA-oleate. Then, the flask was heated up to 120 ^oC with N_2 through and kept for half an hour. Finally, FA-oleate was cooled to 70 ^oC and stored at N_2 atmosphere.

For the synthesis of $CsPbI_3$ QDs: 1 g of PbI_2 and 50 mL of ODE were loaded into a 250 mL three-neck flask, stirring and heating up to 90 ^oC for 1 hour under vacuum. Then, 5 mL OA and 5 mL OAm were injected with constant N_2 flow.The flask was degassed at 90 ^oC for 2 h and then refilled with N_2 and heated up to 160 ^oC. 8 mL of

preheated Cs-oleate in ODE was rapidly injected into the reaction system with constant N_2 flow. The reaction mixture turned into dark red immediately and the flask was quenched by an ice bath after 5 s. When the QD temperature reduced into 50 ^oC, $CsPbI_3$ QDs were transferred into a transferring bottle filled with nitrogen. Then, $CsPbI_3$ QDs were separated into six centrifuge tubes equally, then antisolvent MeOAc with volume ratio of 1:3 (QDs: MeOAc = 1:3 in v:v) was added, centrifuging with speed of 8000 rpm for 5 min. The precipitate was dispersed with 3 mL of n-hexane in each centrifuge tube, and same volume of MeOAc was added afterwards, and again centrifuged at 8000 rpm for 3 min. Finally, the precipitate was dissolved with 20 mL n-hexane and centrifuged at 4000 rpm for 5 min to remove excess PbI_2 and Cs-oleate. The supernatant QDs were stored in dark at 0 °C overnight to precipitate excess Cs-oleate and Pb-oleate. Before use, the QDs were centrifuged at 4000 RPM for 5 min to remove excess precipitate and then dried to achieve QD solids.

For the synthesis of $FAPbI_3$ QDs: The $FAPbI_3$ QDs were synthesized according to our recent report: 0.688 g PbI_2 and 40 mL 1-ODE were degassed under vacuum at 120 °C for 30 min. A mixture of 8 mL of OA and 4 mL of OAm was then injected into the reaction mixture under vacuum. The mixture was degassed under vacuum until the reaction mixture became clear. Under N_2 flow, the temperature was decreased to 80 °C. Then 10 mL as prepared FA-oleate stock solution was then rapidly injected into the reaction flask. After 5 s, the reaction mixture was quenched using an ice-water bath. $FAPbI_3$ QDs were then transferred into a transferring bottle filled with nitrogen. After the mixture cooled to room temperature, 2-pentanol was added (1:1 v:v ratio), and the mixture was centrifuged at 8000 rpm for 5 min. The resulting QD precipitate was dispersed in 14 mL hexane, re-precipitated with mixed ACN/toluene (1:4 v:v ratio), and centrifuged at 8000 rpm for 2 min. After discarding the supernatant, the final precipitate was redispersed in 10 mL of octane and centrifuged at 10000 rpm for 3 min to remove the $FAPbI_3$ clusters. All the purification process was conducted in the N_2 environment. Then the QD solution will be stored in the fridge at 0 ^oC for 24 hours to finally remove excess PbI_2 and FA-oleate. Before use,

the QDs were centrifuged at 10000 RPM for 5 min to remove excess precipitate and then dried to achieve QD solids.

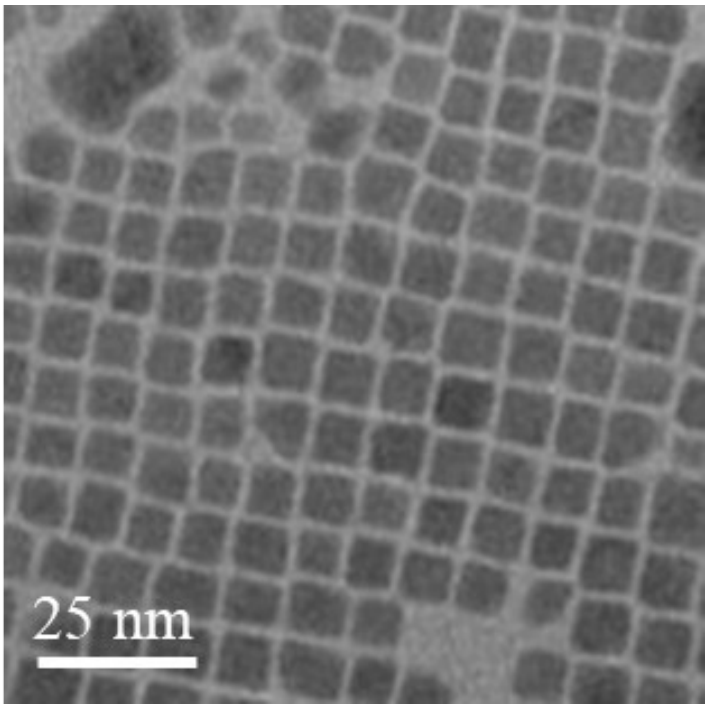

Figure S1. TEM image of $CsPbI_3$ PQDs.

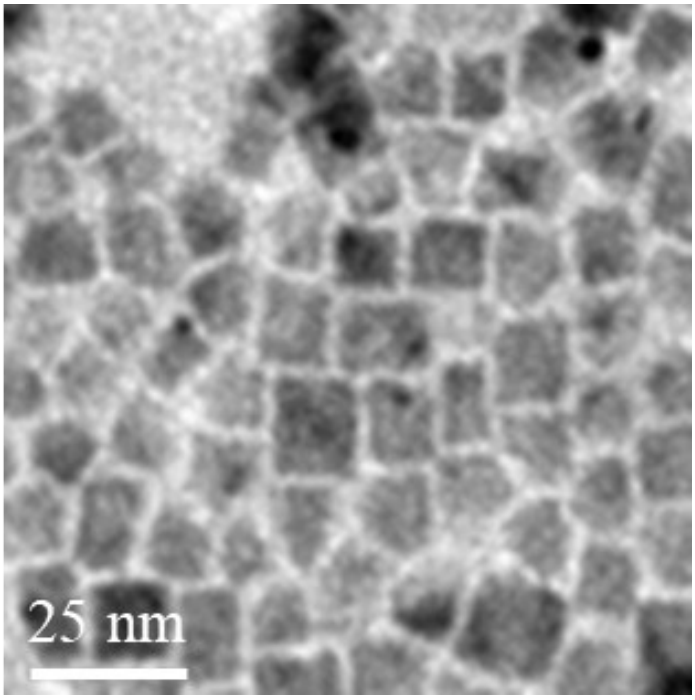

Figure S2. TEM image of $FAPbI_3$ QDs.

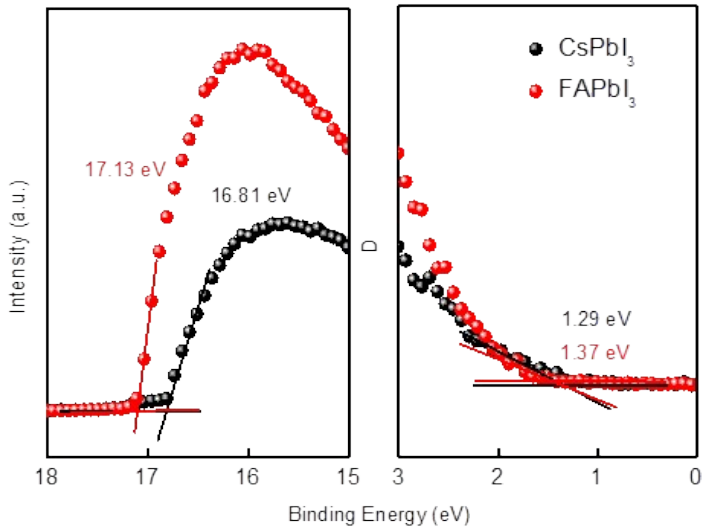

Figure S3. UPS spectra of $CsPbI_3$ and $FAPbI_3$ QD film after MeOAc post-treatment.

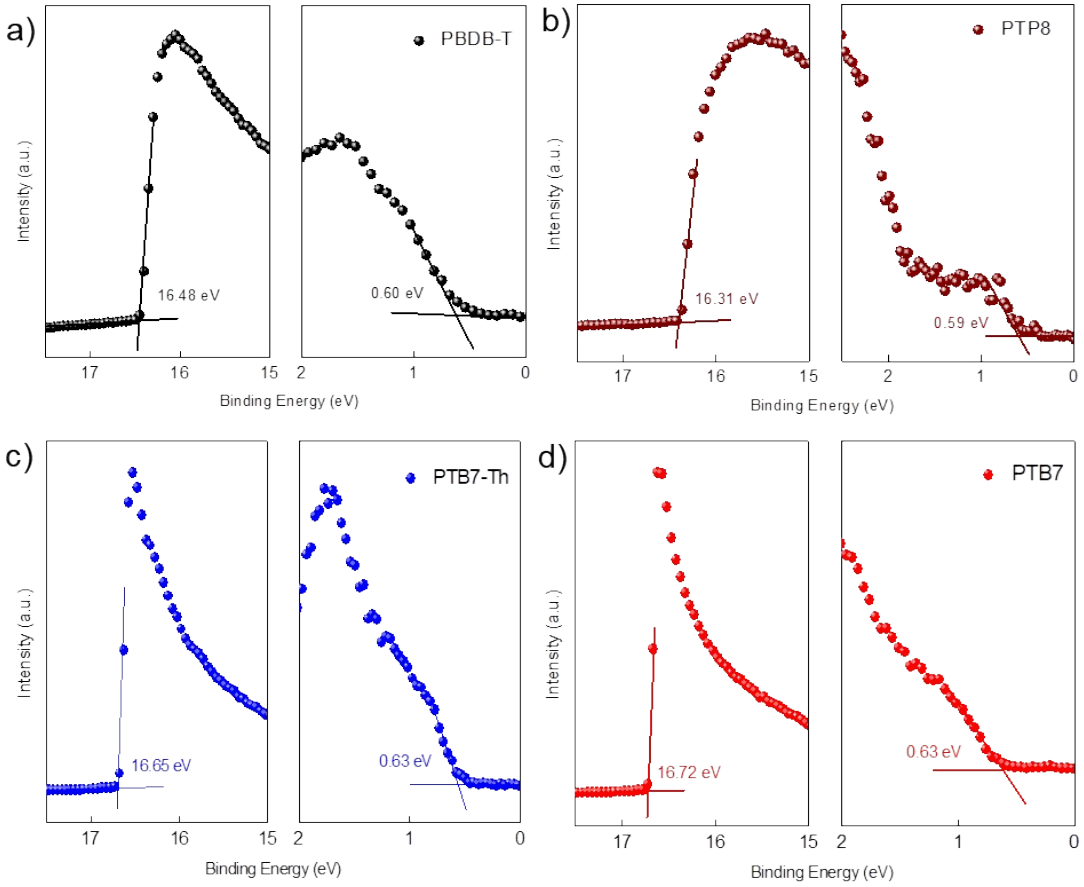

Figure S4. UPS spectra of PBDB-T (a), PTP8 (b), PTB7-Th (c) and PTB7 (d) film.

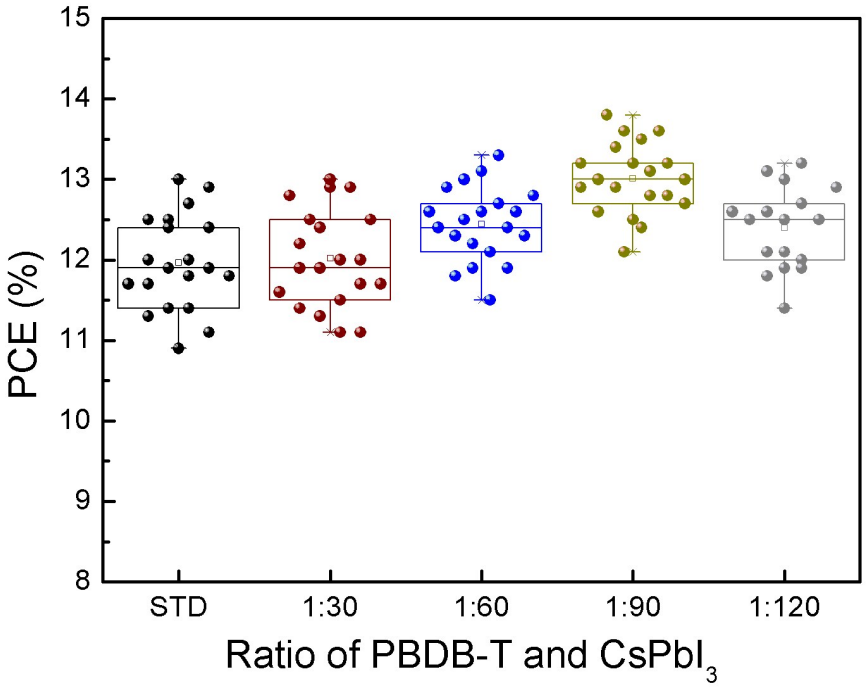

Figure S5. PCE summary of $CsPbI_3$ PQD solar cells devices using PBDB-T/QD hybrid layer with varying blend weight ratios (20 devices for each condition).

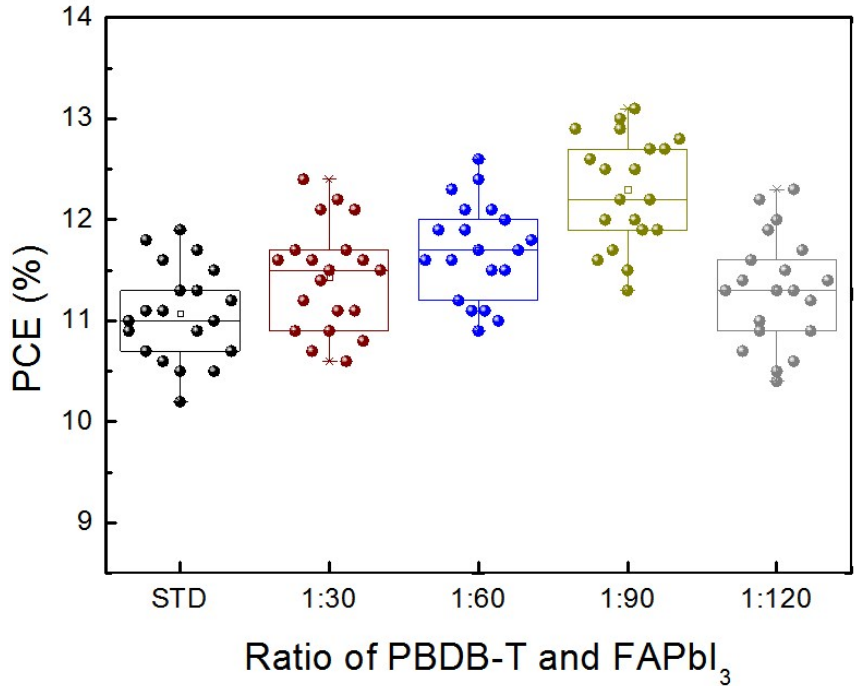

Figure S6. PCE summary of $FAPbI_3$ PQD solar cells devices using PBDB-T/PQD hybrid layer with varying blend weight ratios (20 devices for each condition).

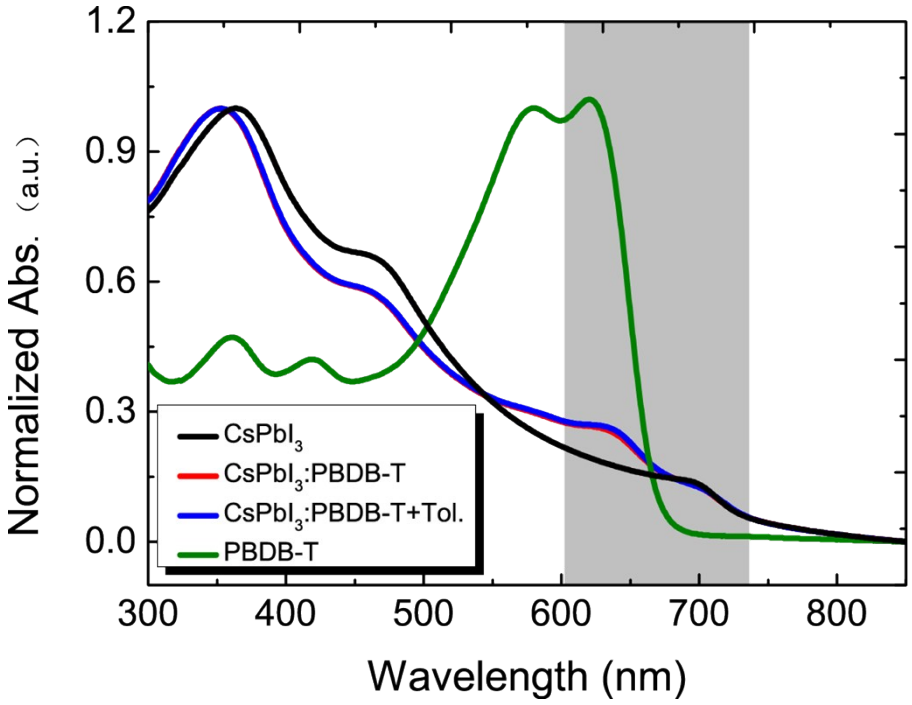

Figure S7. Normalized thin-film absorbance of neat $CsPbI_3$ QDs, PBDB-T+$CsPbI_3$ BHJ, PBDB-T+$CsPbI_3$ BHJ after toluene treatment and pristine PBDB-T.

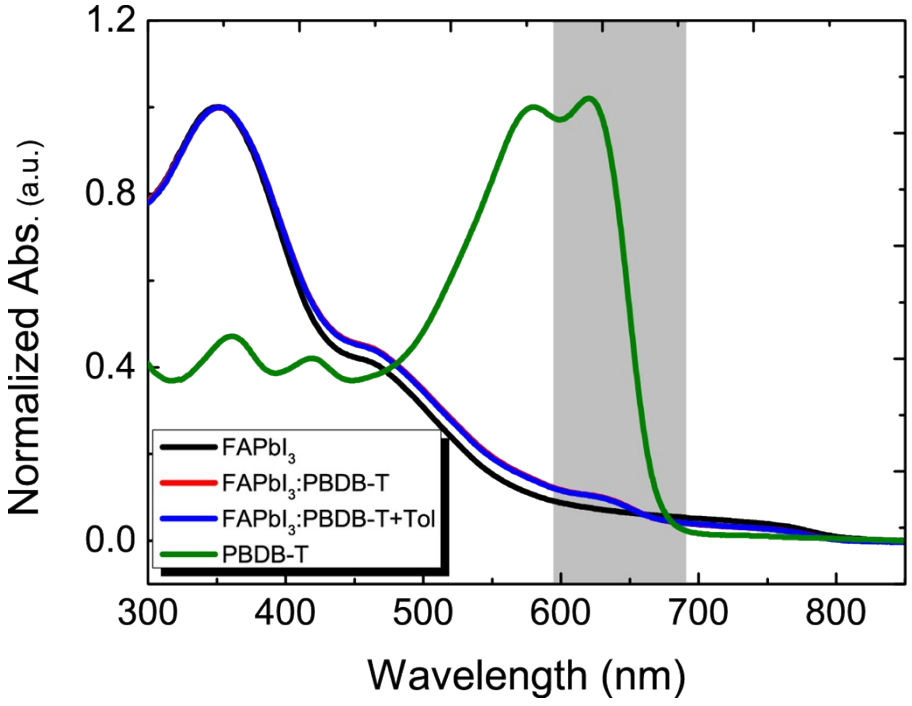

Figure S8. Normalized thin-film absorbance of neat $FAPbI_3$ QDs, PBDB-T+ $FAPbI_3$ BHJ, PBDB-T+ $FAPbI_3$ BHJ after toluene treatment and pristine PBDB-T.

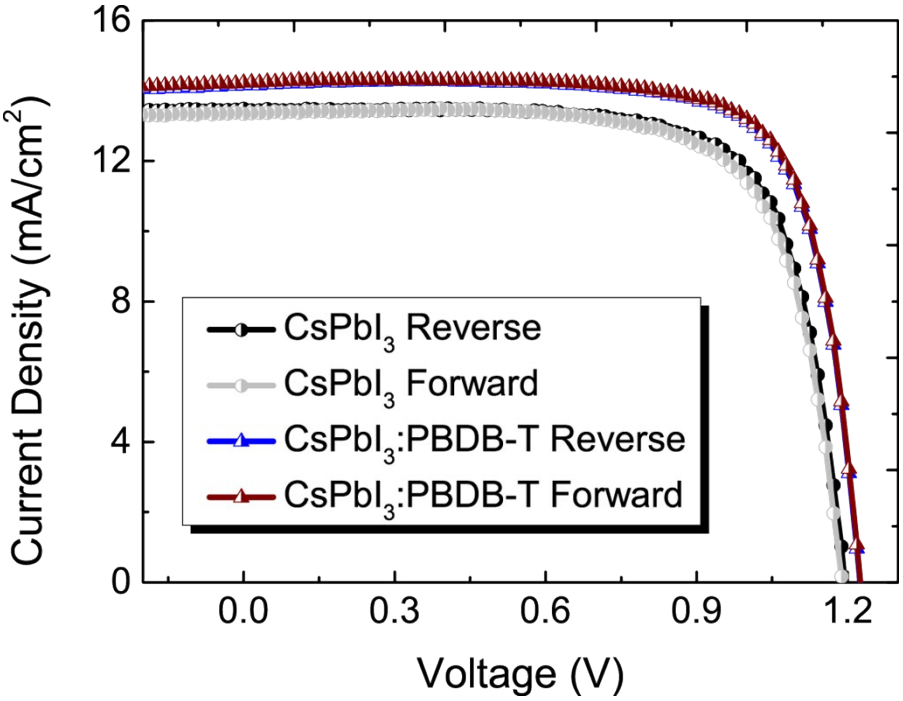

Figure S9. *J-V* curves of forward and reverse scan of $CsPbI_3$ PQD solar cell devices w/wo PBDB-T/QD hybrid layer.

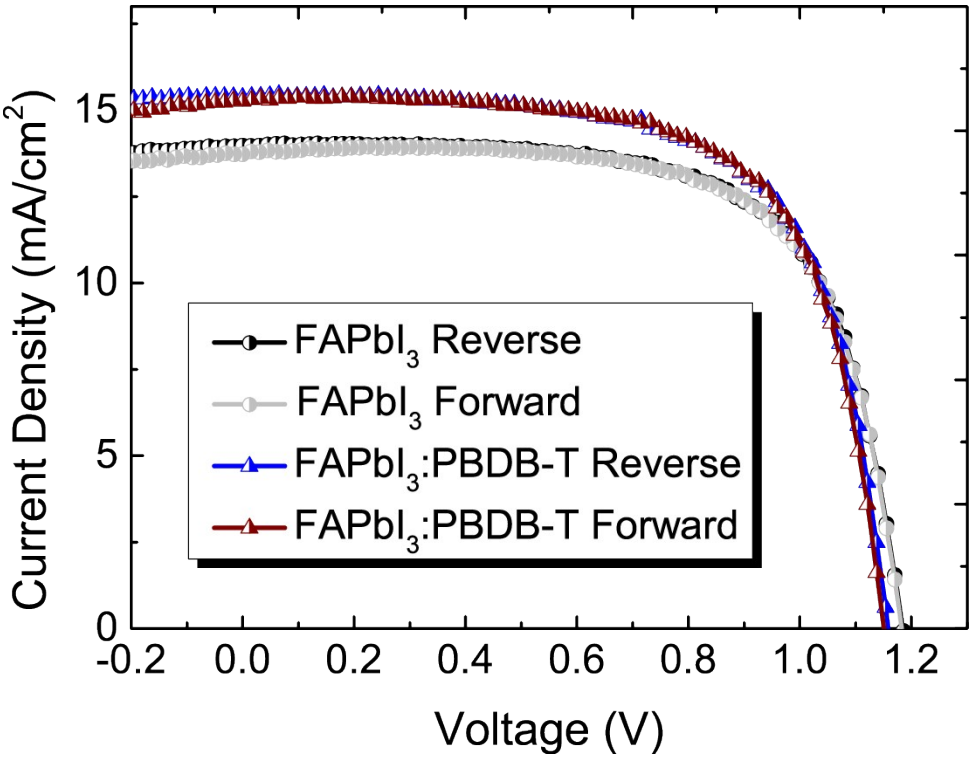

Figure S10. *J-V* curves of forward and reverse scan of neat $FAPbI_3$ PQD solar cell devices w/wo PBDB-T/QD hybrid layer.

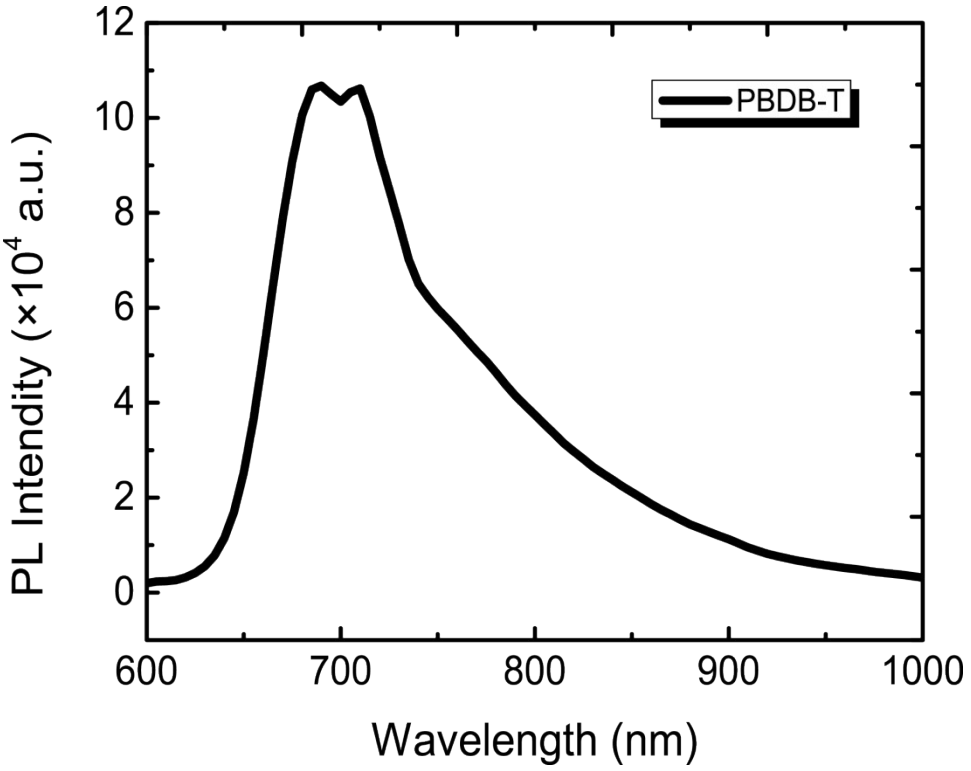

Figure S11.Steady-state photoluminescence (PL) spectrum of neat PBDB-T films

Table S1. Device parameters of $CsPbI_3$ PQD solar cells using PBDB-T/QD hybrid layer with varying blend weight ratios.

PBDB-T:$CsPbI_3$	J_{sc} （mA/cm²）	V_{oc} （V）	FF	PCE (%)
w/o	13.7	1.22	0.77	12.8
1:30	14.5	1.22	0.73	12.9
1:60	14.6	1.22	0.75	13.4
1:90	15.1	1.22	0.75	13.8
1:120	14.0	1.23	0.75	12.9

Table S2. Device parameters of $FAPbI_3$ PQD solar cells using PBDB-T/QD hybrid layer with varying blend weight ratios.

PBDB-T:$FAPbI_3$	J_{sc} （mA/cm^2）	V_{oc} （V）	FF	PCE (%)
w/o	14.0	1.20	0.69	11.6
1:30	16.7	1.13	0.64	12.1
1:60	16.7	1.12	0.68	12.7
1:90	16.7	1.12	0.70	13.2
1:120	15.8	1.14	0.65	11.7

Table S3. Detail data of EIS parameters

Conditions	R_s (Ω)	R_1 (Ω)
$CsPbI_3$	36.36	14690
$CsPbI_3$-PBDB-T	26.72	21620
$FAPbI_3$	50.64	23170
$FAPbI_3$-PBDB-T	30.54	27500

Reference

1. J. Yuan, H. Dong, M. Li, X. Huang, J. Zhong, Y. Li and W. Ma, *Adv. Mater.*, 2014, **26**, 3624-3630.