Tailoring multifunctional anion to inhibit methanol absorption in $CsPbBr_3$ quantum dot surface for highly efficient semitransparent photovoltaics

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Experimental section

Chemicals

All reagents were used as received without further purification. Octadecene (ODE, 90%), oleic acid (OA, 90%), methyl acetate (MeOAc, 99%), chlorobenzene (CB 99.9%) guanidine bromide (GuaBr, 99.5%), guanidinium thiocyanate (GuaSCN, 99.8%), guanidine acetate (GuaAc, 99.5%) were obtained from Sigma-Aldrich., oleylamine (OAm, 90%), and octane (98%) were obtained from Alfa Aesar. PbI_2 (99.99%) and PCBM (99.9%) were obtained from Xi'an Polymer Light Technology Corp. Cs_2CO_3 (99.9%) was obtained from J&K. Spiro-OMeTAD (99.8%) was obtained from Ningbo Borun New Material Co., Ltd. n-hexane (97%), $TiCl_4$ (98%), and ethyl alcohol (≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of $CsPbBr_3$ QDs

The synthesis of $CsPbBr_3$ QDs employed here followed the previously published method. Cesium oleate was prepared by adding ODE (25 mL), Cs_2CO_3 (0.25 g), OA (1 mL) into a 50 mL three-neck flask. It was degassed and dried under vacuum for 30

min at 120 ℃ until a clear solution was obtained.

For the synthesis of $CsPbBr_3$ QDs, $PbBr_2$ (0.4 g), and ODE (25 mL) were loaded into a 50 mL 3-neck flask and heated to 120 °C under vacuum for 30 min, then OA (2.5 mL), OAm (2.5 mL) were injected into the system under the protection of N_2. The flask was put under vacuum again (30 min). The temperature was increased to 170 °C and Cs-oleate solution (4 mL) was quickly injected. After 5 s the solution was immediately cooled down to room temperature by immersing the flask in an ice water bath. The synthesized $CsPbBr_3$ QDs were precipitated by adding 24 ml of MeOAc to 8 ml of the QD reaction liquor (volume ratio of QD reaction solution: MeOAc is 1:3) and then centrifuged at 8500 rpm for 3 min. The wet pellet of QDs in each centrifuge tube was redispersed in 5 mL hexane, precipitated again with 15 mL MeOAc and centrifuged at 8500 rpm for 3 min. The resultant QD pellet was dispersed in 10 ml of hexane and then stored in the dark at 4 °C for at least 24 hours to precipitate excess Cs-oleate and Pb-oleate. Before use, these solid precipitates were removed from the QD solution via centrifugation at 8000 rpm for 3 min.

Fabrication of solar cells

FTO glass is cleaned with deionized water, ethanol, and isopropanol. TiO_2 electron transport layer is prepared by the chemical bath deposition method. Before depositing $CsPbBr_3$ QDs, the FTO/TiO_2 substrates were treated by UV-zone for about 20 min and transferred to a glove box which a relatively-controlled humidity condition from 15% to 20% for efficient ligand exchange. For the fabrication of $CsPbBr_3$ QD films based on solid state ligand exchange, $CsPbBr_3$ QD solution in octane (85 mg/mL) was spin-coated onto the c-TiO_2/FTO substrates at 1000 rpm for 20 s followed by 2500 rpm for 5 s. The as-cast $CsPbBr_3$ QD film was soaked in the ligand solution (the respective ionic salts (GuaBr, GuaSCN, GuaAc) in MeOAc) and spin-dried. And then, the ligand-treated film was washed using neat MeOAc and spin-dried. This process needed to repeat five times to obtain thick enough $CsPbBr_3$ QD film. The as-prepared substrate was transferred to a glove box with pure N_2 to deposit the hole transfer layer. Spiro-MeOTAD used as an HTL in solar cells was spin-coated at 4000 rpm for 30 s.

The spiro-MeOTAD solution was prepared as follows: spiro-MeOTAD (72.3 mg), chlorobenzene (1 mL), 4-tert-butylpyridine (28.8 μL) and Li-TFSI (17.5 μL) solution in acetonitrile with the concentration of 520 mg/mL. In the end, Au electrode (80 nm) was fabricated by thermal evaporation.

Characterization

The transmission electron microscope (TEM) images of $CsPbI_3$ QDs were obtained by JEM-2100F. The optical properties of the samples were measured by an UV–vis spectrophotometer (UV-2550). The steady-state PL and PLQY were obtained by HoribaFluoroMax-4 fluorescence spectrometer. XRD patterns of perovskite films and QDs were measured using PANalytical X-Rert PRO MPD. Top-view surface morphology of films was performed using Gemini 500. XPS spectra were recorded using an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi). AFM topography images were acquired on a Bruker Dimension Icon instrument. The photocurrent density-voltage (*J-V*) characteristics of solar cells were measured under AM 1.5G illumination at 100 mW/cm^2 (Newport Sol3A solar simulators) using a Keithley 2450 source meter.

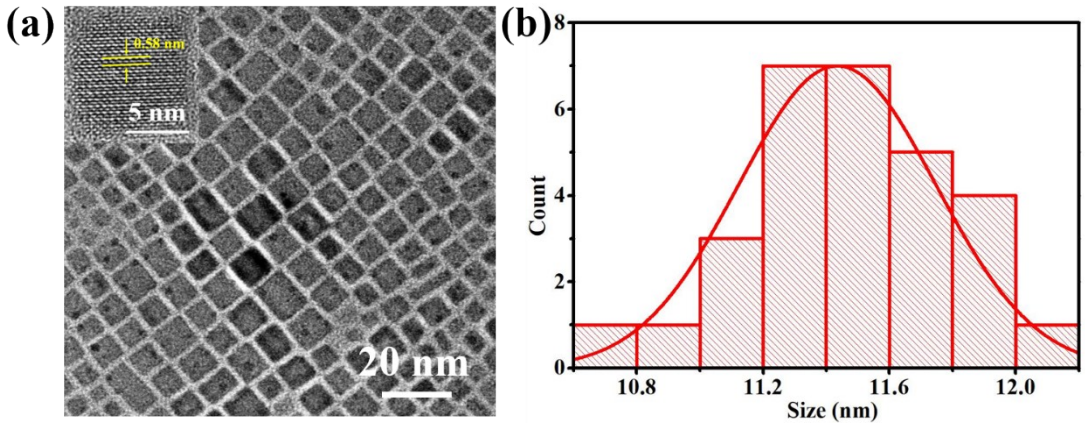

Figure S1. a) TEM image of purified $CsPbBr_3$ QDs with an average size around 10 nm. b) The corresponding particle size distributions

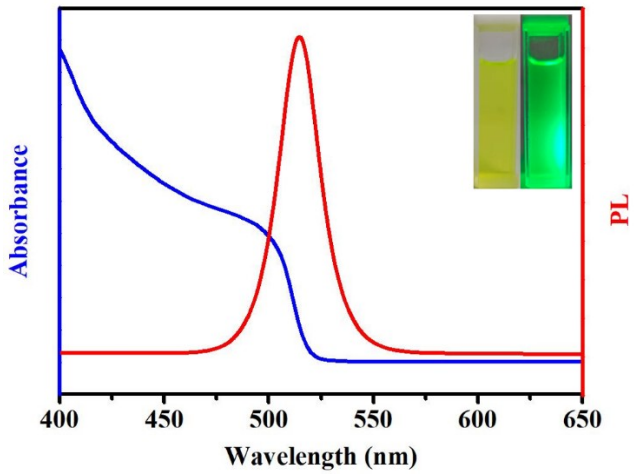

Figure S2. UV-vis absorption and PL spectra of $CsPbBr_3$ QD solution in hexane.

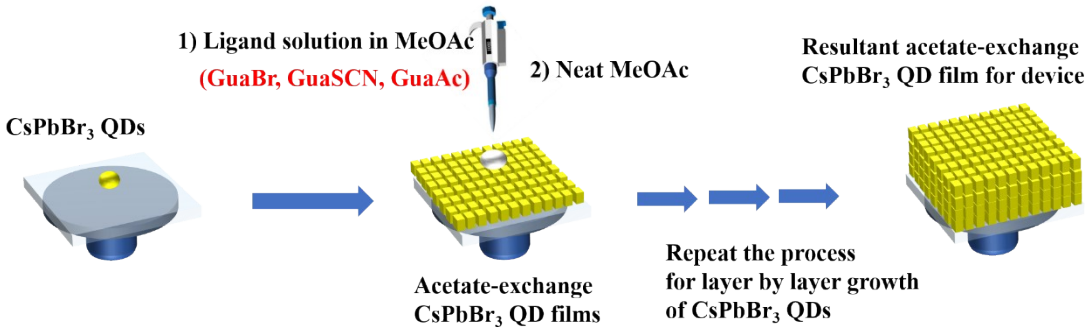

Figure S3. $CsPbBr_3$ QD solid fabrication using solid-state ligand exchange based on layer-by-layer process.

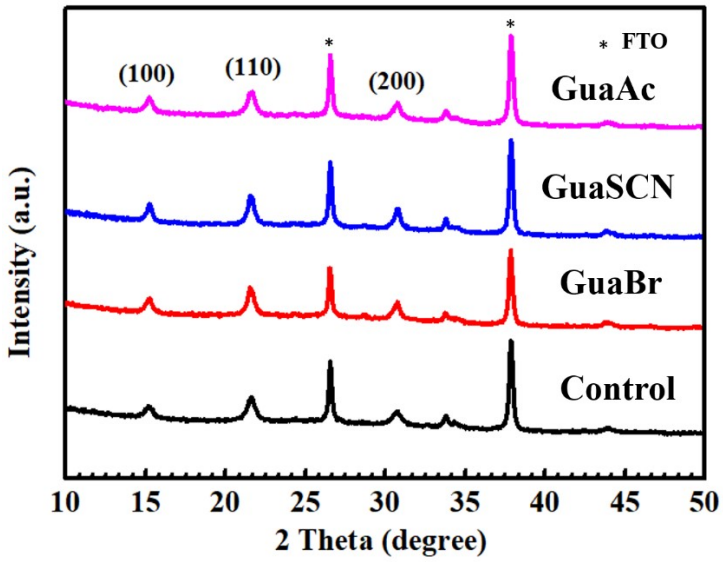

Figure S4. XRD patterns of $CsPbBr_3$ QD films with and without GuaBr, GuaSCN and GuaBr treatment.

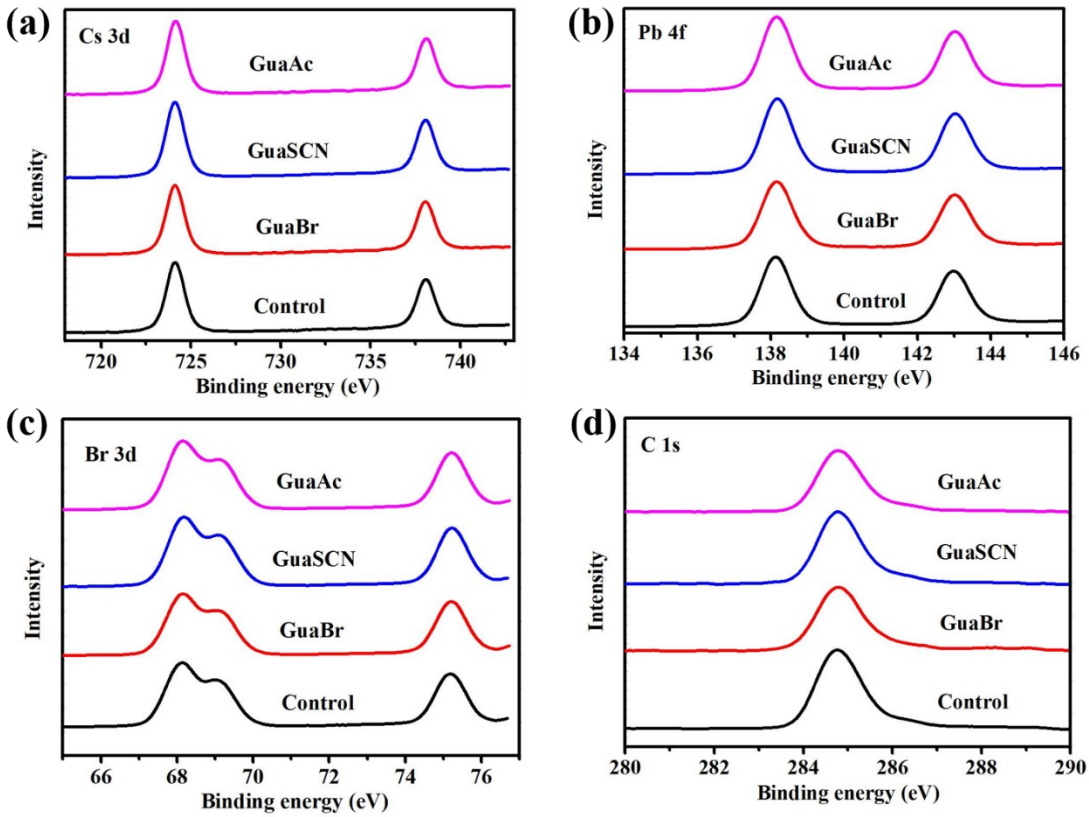

Figure S5. XPS (a) Cs 1s, (b) Pb 4f, (c) Br 3d and (d) C 1s of $CsPbBr_3$ QD films with and without GuaBr, GuaSCN, GuaAc treatment.

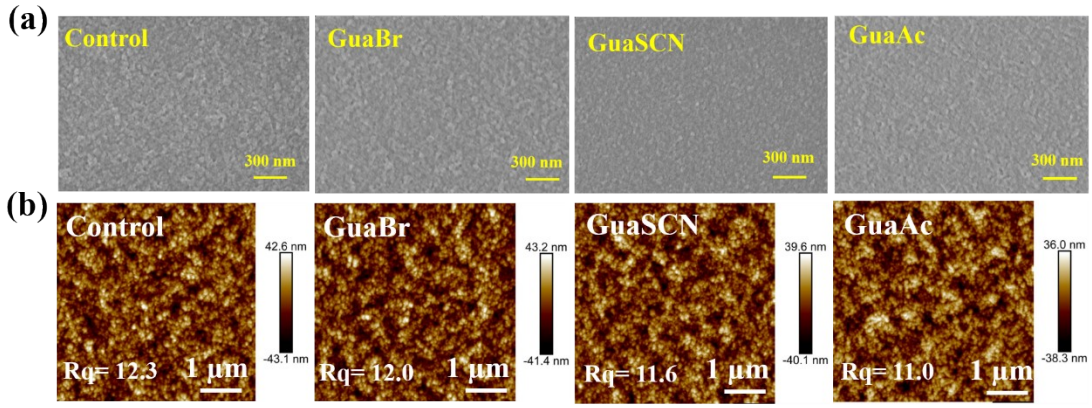

Figure S6. a) The top-view SEM, b) AFM height images of $CsPbBr_3$ QD films with and without GuaBr, GuaSCN and GuaAc treatment.

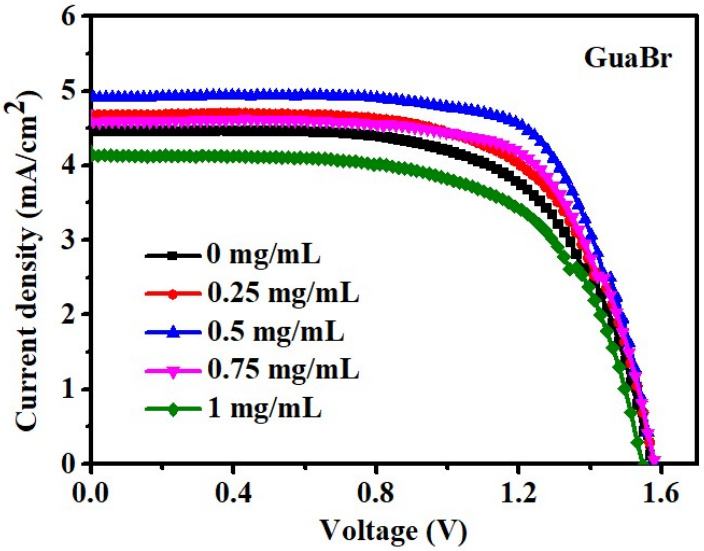

Figure S7. *J-V* characteristic curve of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaBr in MeOAc (0, 0.25, 0.5, 0.75, 1 mg/mL).

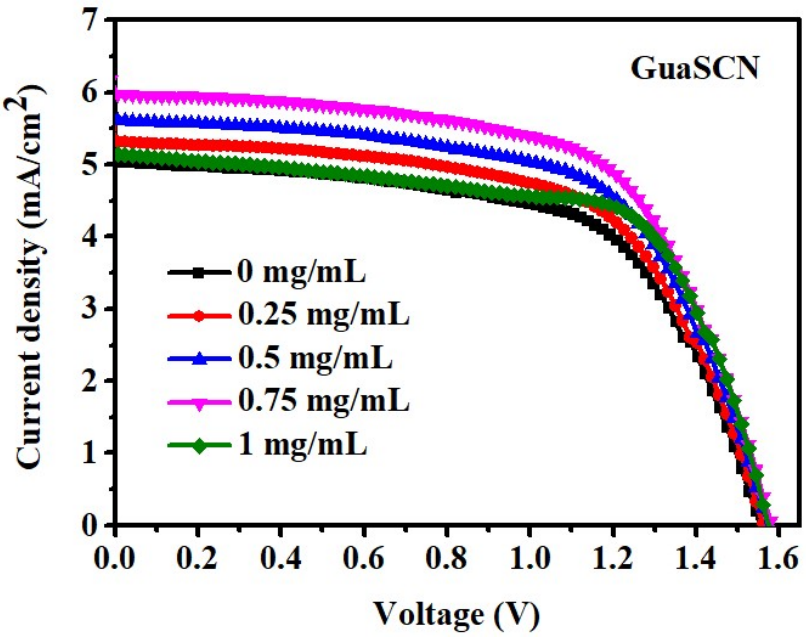

Figure S8. *J-V* characteristic curve of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaSCN in MeOAc (0, 0.25, 0.5, 0.75, 1 mg/mL).

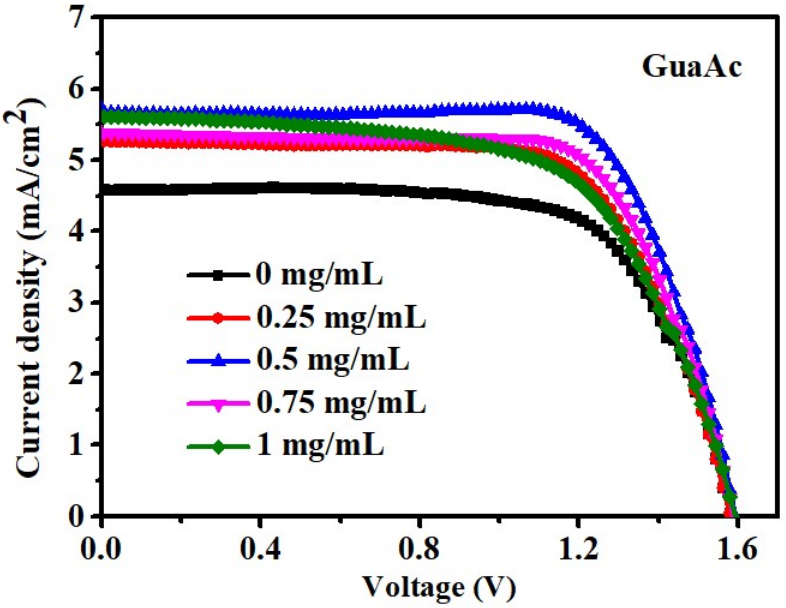

Figure S9. *J-V* characteristic curve of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaAc in MeOAc (0, 0.25, 0.5, 0.75, 1 mg/mL).

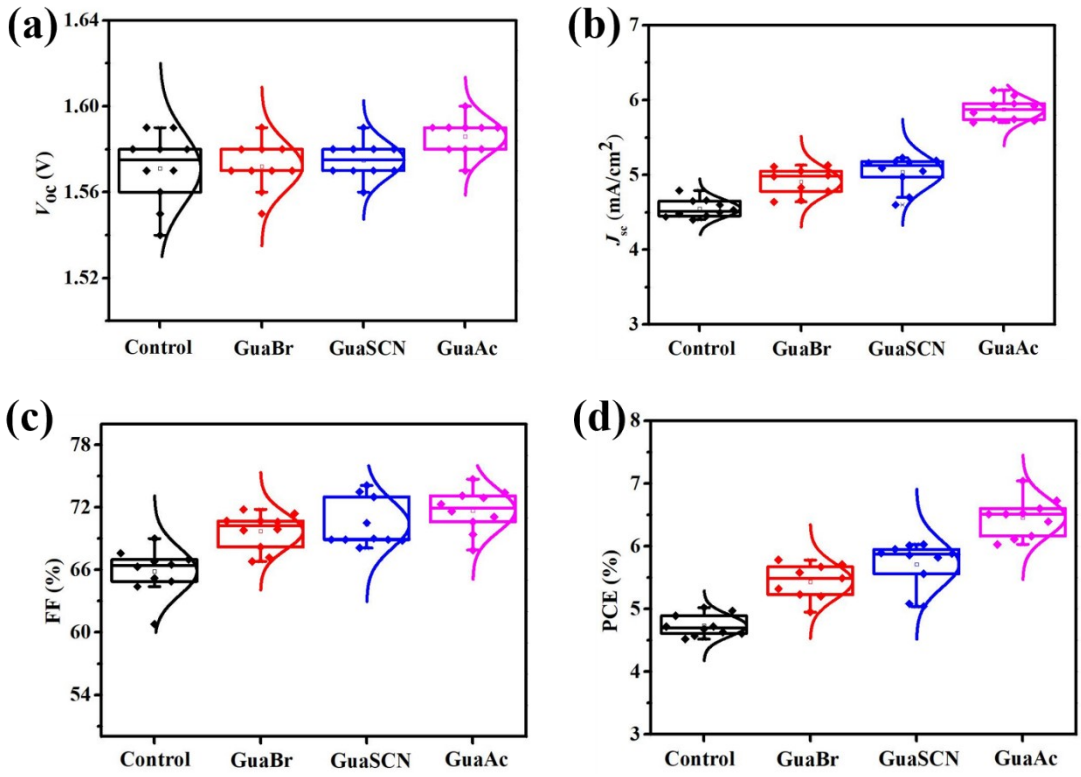

Figure S10. Statistics on photovoltaic parameters of V_{OC}, J_{SC}, FF, and PCE of $CsPbBr_3$ QD solar cell with and without GuaBr, GuaSCN, GuaAc treatment.

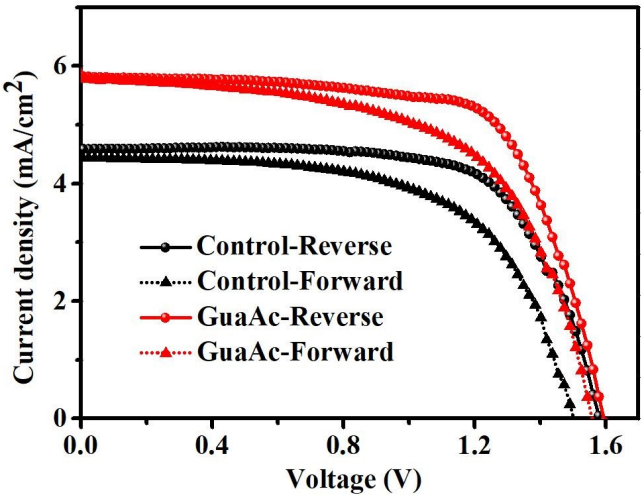

Figure S11. *J-V* curves of $CsPbBr_3$ solar cells with and without GuaAc treatment under reverse and forward scan.

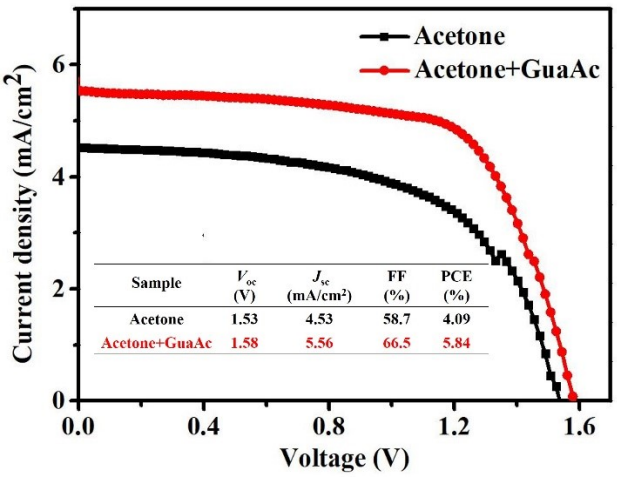

Figure S12. *J-V* curves of $CsPbBr_3$ QD solar cells based on acetone and acetone + GuaAc treatment.

Table S1 Photovoltaic parameters of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaBr.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
0 mg/mL	1.57	4.48	64.4	4.52
0.25mg/mL	1.58	4.68	65.3	4.83
0.5 mg/mL	1.58	4.91	70.6	5.48
0.75 mg/mL	1.56	4.61	69.0	5.02
1 mg/mL	1.54	4.16	64.1	4.12

Table S2 Photovoltaic parameters of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaSCN.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
0 mg/mL	1.55	5.08	61.2	4.83
0.25mg/mL	1.56	5.35	61.2	5.11
0.5 mg/mL	1.57	5.62	62.0	5.48
0.75 mg/mL	1.58	5.93	61.8	5.88
1 mg/mL	1.57	5.15	65.8	5.34

Table S3 Photovoltaic parameters of $CsPbBr_3$ QD solar cells treated with different concentrations of GuaAc.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
0 mg/mL	1.58	4.60	69.0	5.02
0.25mg/mL	1.58	5.27	69.1	5.76
0.5 mg/mL	1.59	5.69	72.9	6.61
0.75 mg/mL	1.58	5.41	70.8	6.07
1 mg/mL	1.59	5.62	62.8	5.61

Table S4 Photovoltaic parameters of $CsPbBr_3$ QD solar cells with and without GuaBr, GuaSCN and GuaAc treatment

Sample	V_{oc} **(V)**	J_{sc} **(mA/cm²)**	**FF (%)**	PCE_{max} **(%)**
Control	1.58	4.60	69.0	5.02
GuaBr	1.57	5.18	71.1	5.82
GuaSCN	1.58	5.23	72.9	6.03
GuaAc	1.59	5.93	74.7	7.04