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Supplementary information

Surface Co-modification Enabling Efficient and Spectrally Stable Mixed-halide Blue Light-emitting Diodes

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Experimental Section

Materials

$PbBr_2$ (99.99%), $PbCl_2$ (99.99%), Na_2CO_3 (99.99%) and n-Octanoic acid (OTA) (99%) were purchased from Macklin. Cs_2CO_3 (99.9%), Rb_2CO_3 (99.5%), Tetraoctylammonium bromide (TOAB) (98%), Didodecyldimethylammonium bromide (DDAB) (98%), n-Octane (99%) and Ethylacetate (99%) were purchased from Aladdin. O-Diphenylphosphinylhydroxylamine (DPH) (98%), Toluene (99.8%) and FA(AC) (99%) were provided by Bidepharm, Dmreagent and Innochem, respectively. TPBi, Poly-TPD were purchased from Xi'an Polymer Light Technology Corp. PEDOT:PSS, LiF and Al were all purchased from Luminescence Technology Corp. All materials were used directly without further purification.

Synthesis and purification of perovskite quantum dots

0.1 M Cs_2CO_3, Na_2CO_3, Rb_2CO_3 and 0.2 M FA(AC) were prepared in OTA, and Cs_2CO_3, Na_2CO_3, Rb_2CO_3 and FA(AC) were mixed into solution A at a volume ratio of 28 : 10 : 2 : 7. Pb precursor solution was formed by adding 0.075 mmol $PbBr_2$, 0.05 mmol $PbCl_2$ and 0.33 mmol TOAB into toluene. 1 mL of solution A was quickly injected into 5 mL of Pb precursor solution for 30 s, followed by 1.7 mL of DDAB for a two-minute reaction. After the reaction was completed, 14 mL of ethyl acetate was added to the mother liquor to remove the unreacted raw materials and excess ligands, and the mixture was dissolved in 2 mL of toluene after centrifugation at 10000 rpm for 2 minutes. 4 mL of ethyl acetate was added again, centrifuged at 10000 rpm for 2 minutes, and finally dissolved in n-octane for the manufacture of the device. The synthesis of DPH-treated QDs only needs to add different amounts of DPH to the precursor solution of Pb and DDAB.

Device fabrication

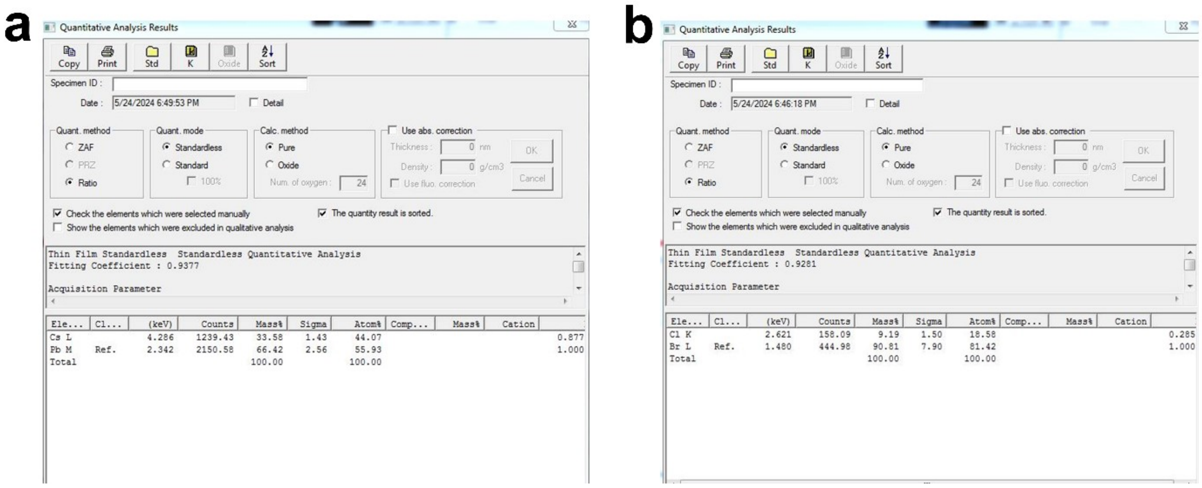
The cleaned ITO glass was treated with plasma for 15 minutes. PEDOT:PSS was spun on the ITO substrate at 5000 rpm and then annealed at 150 ℃ for 10 minutes. Subsequently, (8 mg/mL) Poly-TPD was spun on PEDOT:PSS in the glovebox at 3000 rpm and then annealed at 120 ℃ for 10 minutes. QD solution was spun on poly-TPD without annealing. Finally, (70 nm) TPBi, (1 nm) LiF, and (100 nm) Al were deposited below a pressure of 8×10^{-4} Pa.

Characterization

Transmission electron microscopy (TEM) and corresponding elemental mapping images were measured using JEM-2800 at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained by Rigaku Smart Lab 3kW in the 2θ ranging from 10 to 50 degrees operating with Cu kα (λ = 1.5406 Å). The absorption spectra was obtained by UV-2600. The photoluminescence (PL) emission spectra, photoluminescence quantum yield (PLQY) and time-resolved photoluminescence (TRPL) decay of QD solution were acquired via FS5. Transient absorption (TA) measurements were recorded on a Time-Tech Spectra transient absorption spectrometer (TA100). Fourier transform infrared spectroscopy (FTIR) was measured using TENSOR 37. Nuclear magnetic resonance (NMR) was conducted using AVANCE III HD 400 MHz. X-ray photoelectron spectroscopy (XPS) was measured using Thermo Scientific ESCALAB 250Xi. The film morphology and roughness were characterized by Dimension Icon. Field emission scanning electron microscope (SEM) images were conducted using JSM-7800F.The J-V and L-V curves and electroluminescence (EL) spectra were measured using PR-735 optical test system. The external quantum efficiency (EQE) is calculated by the following formula:[1]

$$EQE = \eta_A \frac{\pi q}{683hc} \frac{\int_{380\,nm}^{800\,nm} I(\lambda)d\lambda}{\int_{380\,nm}^{800\,nm} I(\lambda)V(\lambda)d\lambda}$$

Where η_A is the current efficiency; $I(\lambda)$ is the intensity of EL spectrum signal; $V(\lambda)$ is 1924 CIE standard visual efficiency function.



a

Specimen ID :

Date : 5/24/2024 6:49:53 PM ☐ Detail

Quant. method: ○ ZAF ○ PRZ ● Ratio

Quant. mode: ● Standardless ○ Standard ☐ 100%

Calc. method: ● Pure ○ Oxide Num. of oxygen : 24

☐ Use abs. correction Thickness : 0 nm Density : 0 g/cm3 ☐ Use fluo. correction OK Cancel

☑ Check the elements which were selected manually ☑ The quantity result is sorted.

☐ Show the elements which were excluded in qualitative analysis

```
Thin Film Standardless  Standardless Quantitative Analysis
Fitting Coefficient : 0.9377

Acquisition Parameter
```

```
Ele...  Cl...    (keV)    Counts   Mass%   Sigma   Atom%  Comp...   Mass%   Cation
Cs L             4.286   1239.43   33.58    1.43   44.07                               0.877
Pb M    Ref.     2.342   2150.58   66.42    2.56   55.93                               1.000
Total                             100.00          100.00
```

b

Specimen ID :

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Quant. mode: ● Standardless ○ Standard ☐ 100%

Calc. method: ● Pure ○ Oxide Num. of oxygen : 24

☐ Use abs. correction Thickness : 0 nm Density : 0 g/cm3 ☐ Use fluo. correction OK Cancel

☑ Check the elements which were selected manually ☑ The quantity result is sorted.

☐ Show the elements which were excluded in qualitative analysis

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Thin Film Standardless  Standardless Quantitative Analysis
Fitting Coefficient : 0.9281

Acquisition Parameter
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Cl K             2.621    158.09    9.19    1.50   18.58                               0.285
Br L    Ref.     1.480    444.98   90.81    7.90   81.42                               1.000
Total                             100.00          100.00
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Fig. S1 The elemental ratios of Cs to Pb and Br to Cl.

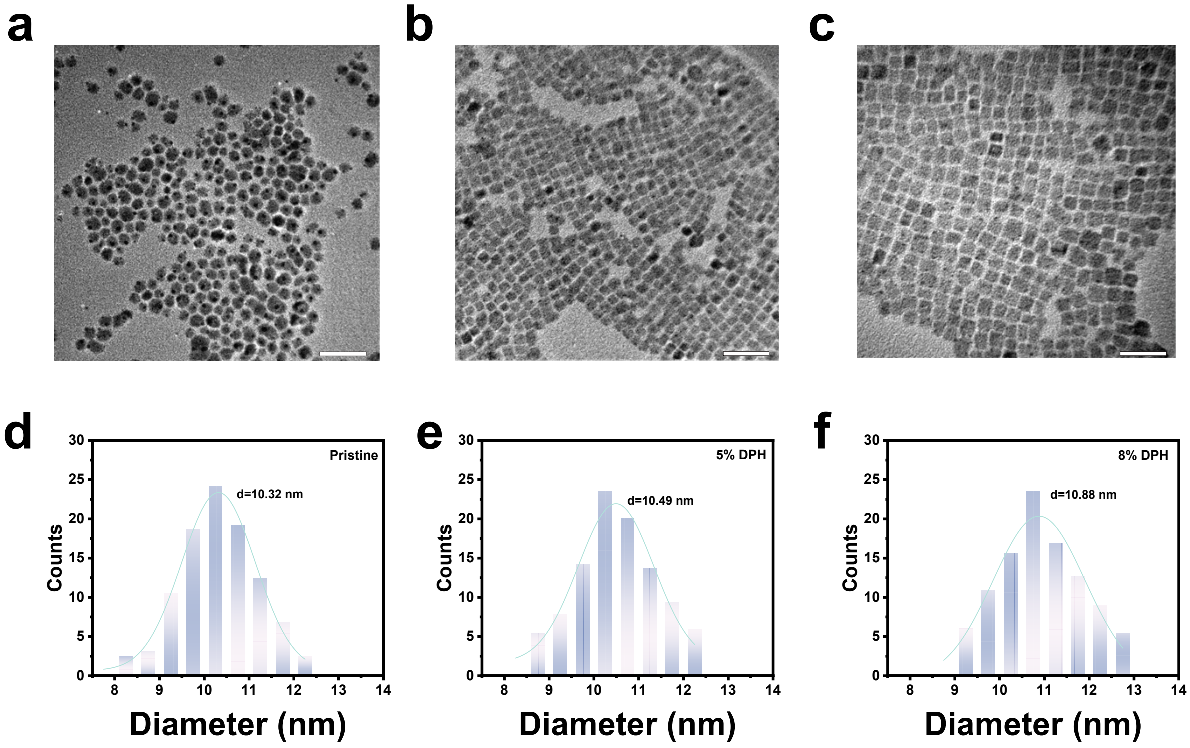

Fig. S2 TEM images and size distribution of a) pristine，b) 5%，c) 8% DPH-treated QDs.

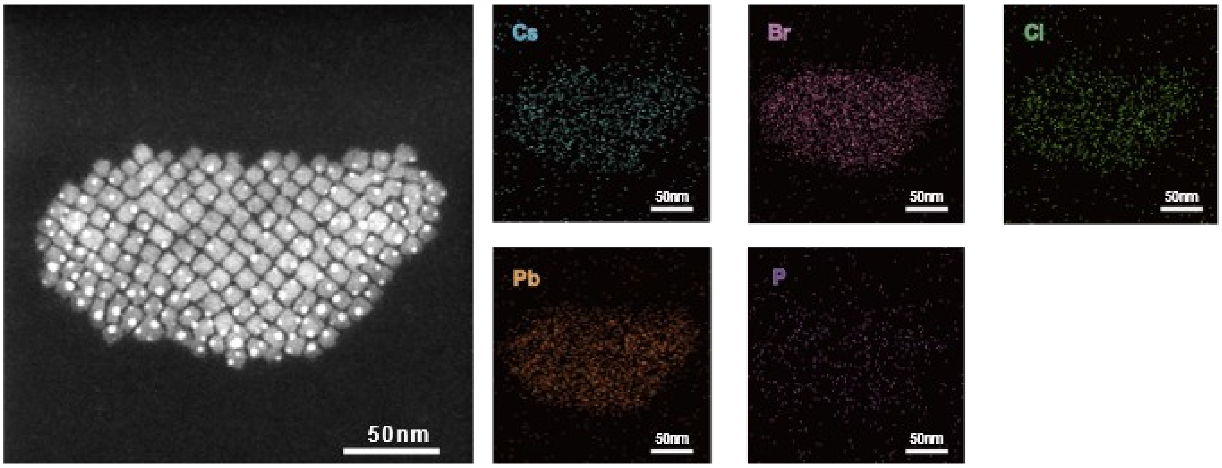

Fig. S3 HAADF-STEM images and corresponding elemental mapping of the treated QDs.

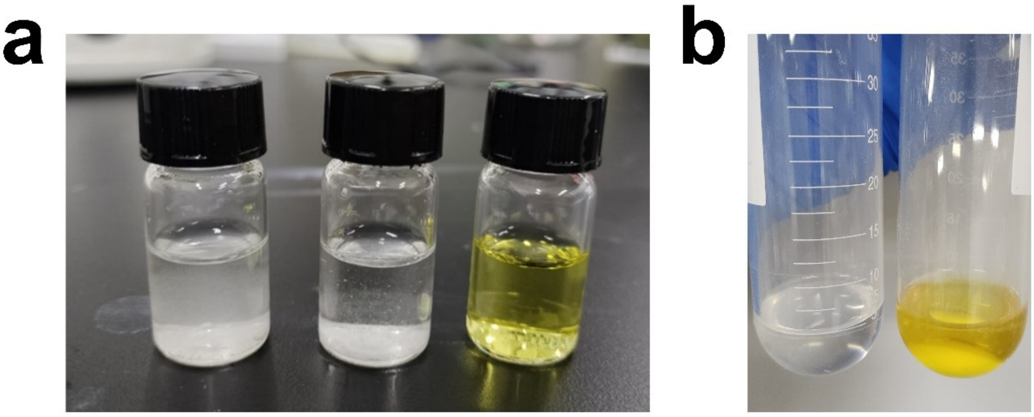

Fig. S4 The picture of pure DPH, mixture of DPH and $PbBr_2$, and mixture of DPH and HBr in 2 mL of anhydrous ethanol, respectively.

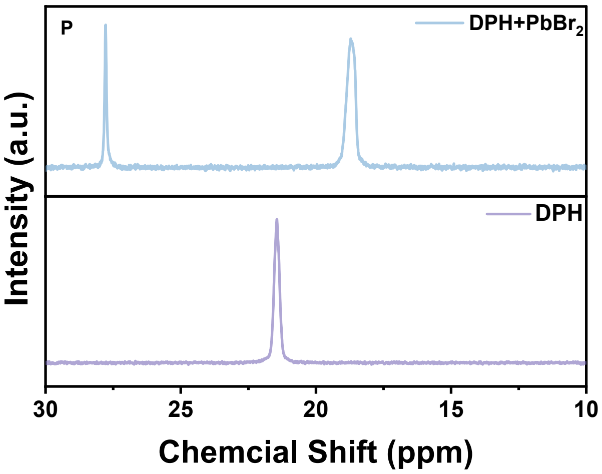

Fig. S5 NMR spectra of DPH and DPH with $PbBr_2$.

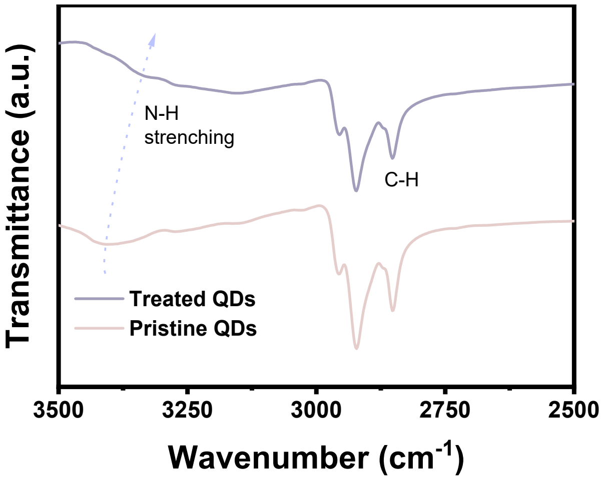

Fig. S6 FTIR spectra of the pristine and treated QDs.

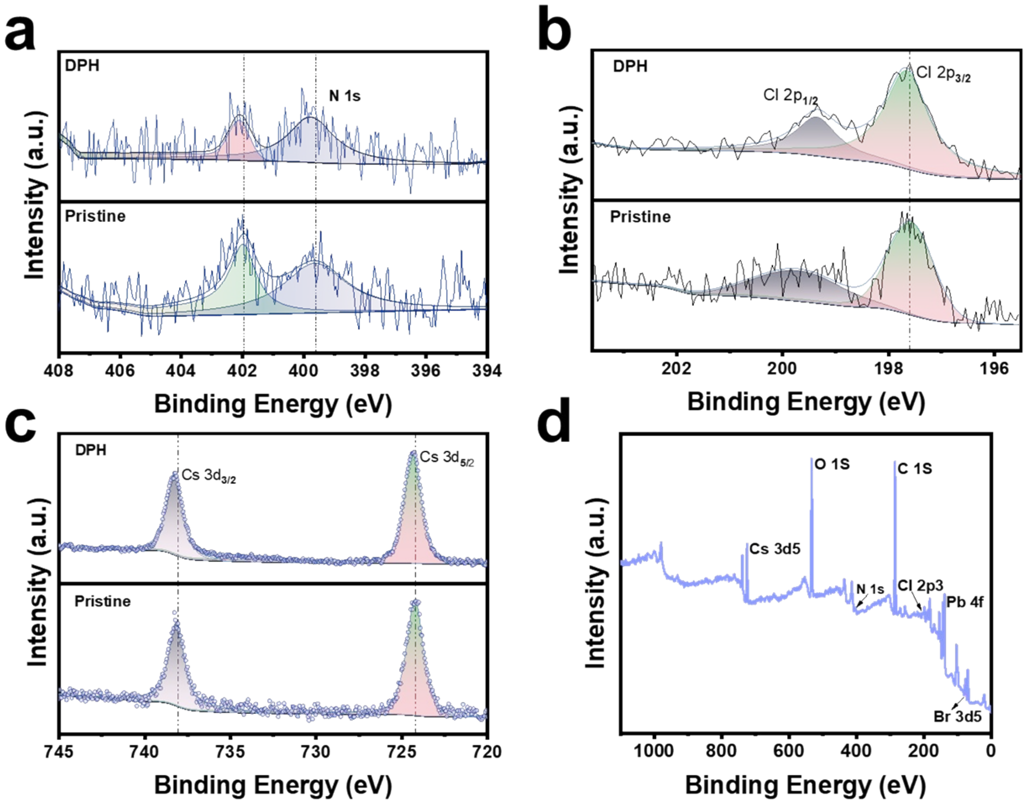

Fig. S7 XPS spectra of the pristine and DPH-treated QDs for a) N 1s, b) Cl 2p, c) Cs 3d, d) survey.

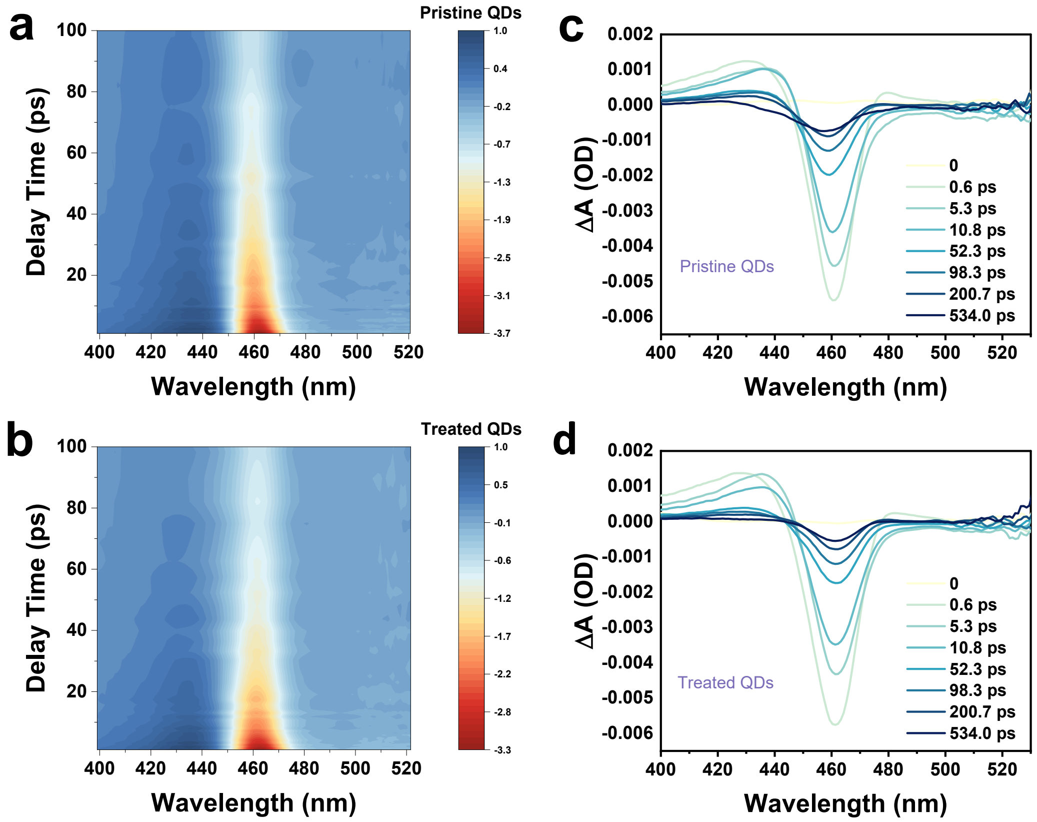

Fig. S8 TA spectra of a) pristine and b) treated QDs films over delay time. TA spectra of c) pristine and d) treated QD films within a certain time scale.

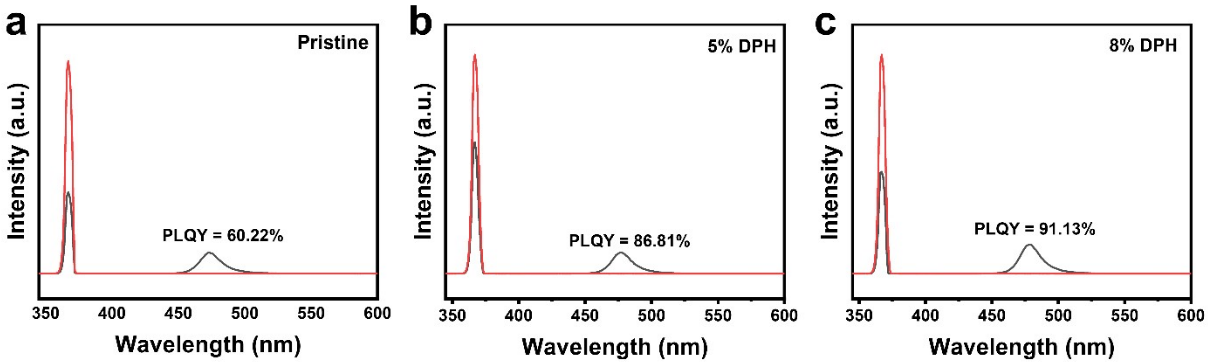

Fig. S9 PLQY measurements of (a) the pristine QDs and (b) 5% DPH-treated QDs, (c) 8% DPH-treated QDs.

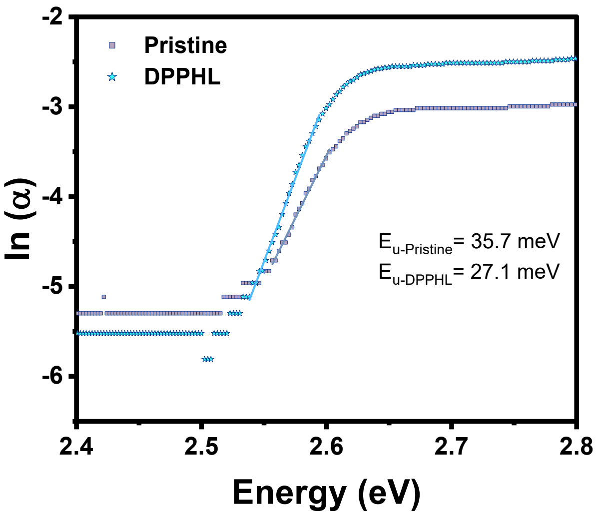

Fig. S10 Urbach energies of the pristine and treated QDs.

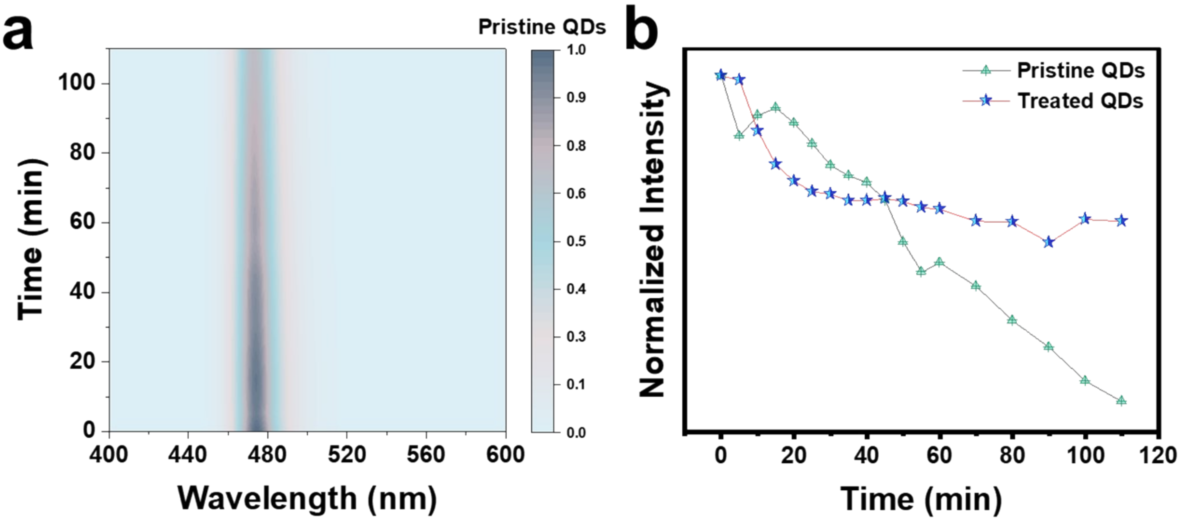

Fig. S11 Stability of emission spectrum of the pristine and treated QDs solutions under 365nm UV light.

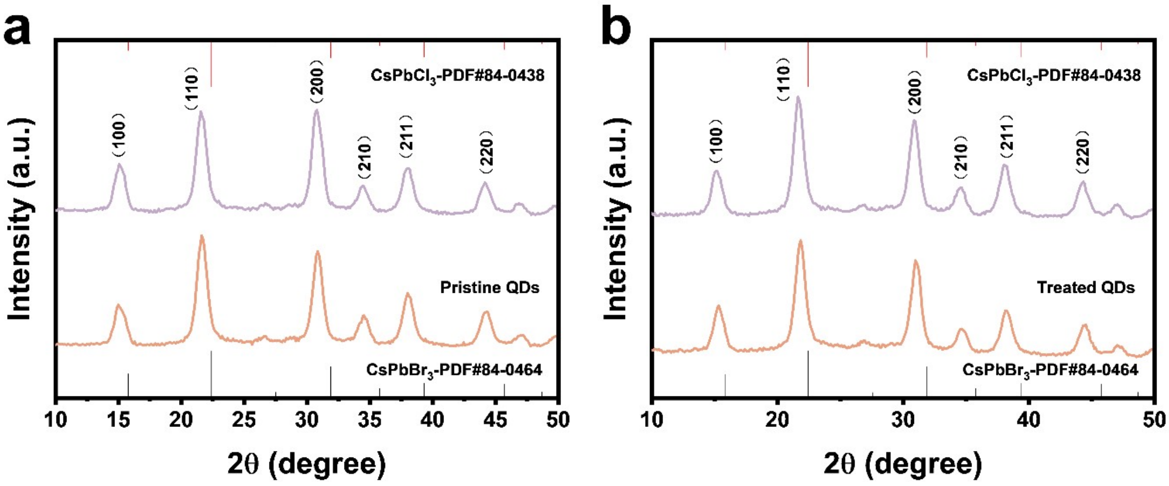

Fig. S12 XRD patterns of pristine QDs and treated QDs before and after UV illumination for 2h (365 nm).

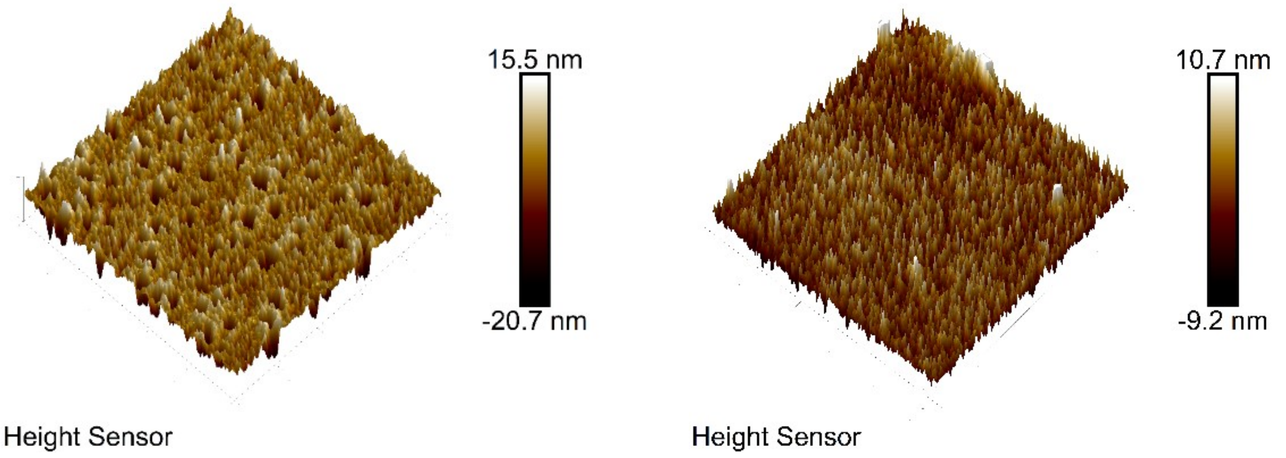

Fig. S13 AFM images of the pristine and treated QDs.

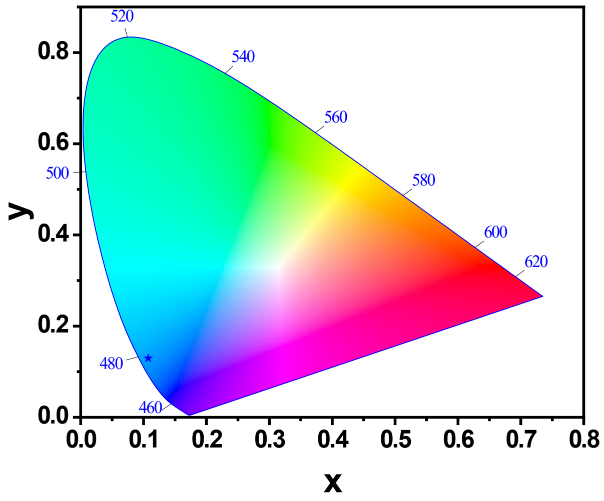

Fig. S14 CIE coordinates of the target PeLEDs.

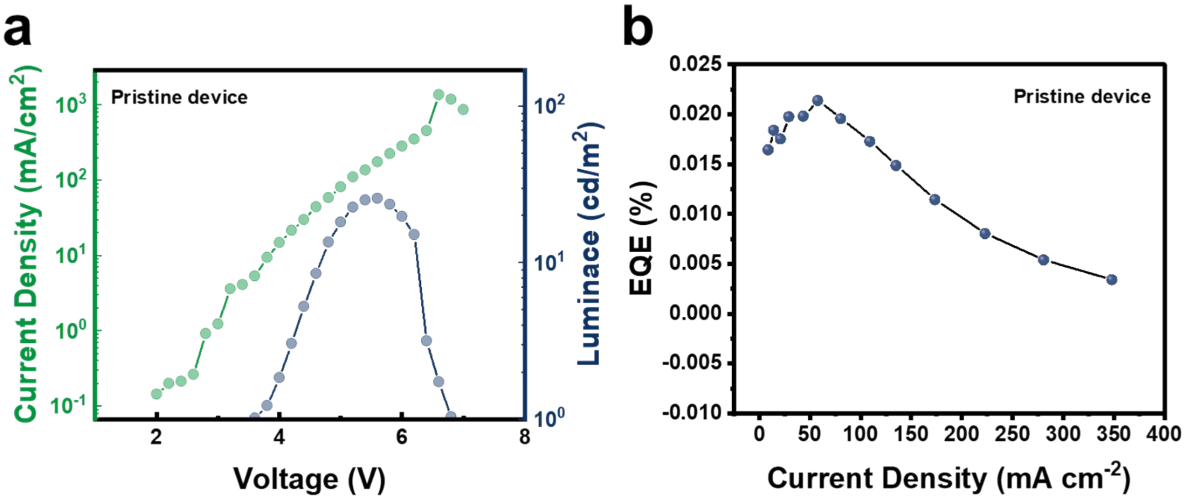

Fig. S15 a) Current density–voltage–luminance curves, b) current density-EQE curves of the treated PeLEDs.

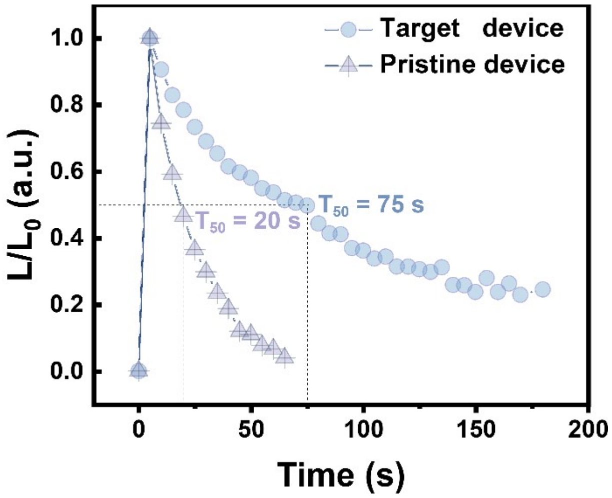

Fig. S16 Luminance decay of the pristine and target device operating in initial luminance of about 100 cd/m^2 (Target device) and 30 cd/m^2 (Pristine device).

Table S1. Fitted elemental contents of pristine and treated QDs by XPS.

Element	**C**	**O**	**Cs**	**Pb**	**Br**	**Cl**	**N**	**P**
Pristine	75.30	20.57	0.38	0.47	1.66	0.58	1.04	0
Treated	69.10	26.07	0.52	0.58	1.89	0.57	0.73	0.54

Table S2. Summary of time-resolved PL fitting parameters of pristine, 5%, 8% DPH-treated QDs.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{ave} (ns)	K_{nonrad} (μs^{-1})	K_{rad} (μs^{-1})
Pristine	420.88145	3.26996	1091.37525	17.80714	452.16968	64.74537	44.84343654	8.870863401	13.42894404
5% DPH	449.39387	4.52697	1155.79813	20.51883	375.94413	66.10418	42.26383165	3.120871792	20.54002125
8% DPH	463.07809	4.32123	1208.17392	18.8454	346.2488	62.12596	38.33402934	2.313871031	23.77261184

Reference

1 M. Shukla, N. Brahme, R. S. Kher, M. S. K. Khokhar, Elementary approach to calculate quantum efficiency of polymer light emitting diodes, *Indian J. Pure Appl. Phys.*, 2011, **49**, 142-145.