

Supporting Information

Water-stable and ion exchange-free inorganic perovskite quantum dots encapsulated in solid paraffin and their application in light emitting diodes

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Experimental section

Materials: Cesium carbonate (Cs_2CO_3 , 99%), lead bromide (PbBr_2 , 99%), lead iodide (PbI_2 , 98%), lead chloride (PbCl_2 , AR), 1-octadecene (ODE, 90%), oleic acid (OA, AR), oleylamine (OAm, 80%–90%), paraffin (P, Pathological grade) with melting point (MP) of 60 °C were purchased from Aladdin. BARECO PX-105 Fischer-Tropsch wax with MP of 105 °C was available from Shell MDS (Malaysia). All reagents were used as received without further purification. Commercial UV LED chips with aluminum sinks were obtained from a local supplier.

Apparatus: UV/vis absorption spectra were measured by a spectrophotometer (TU-1950, Persee). Fluorescence spectra were obtained on a F-4600 fluorescence spectrophotometer (Hitachi). LED spectra were recorded with a USB2000 fluorescence spectrometer (Ocean Optic Inc., USA). XRD measurements were carried out on a Rigaku D/MAX 2200 VPC using a Cu K α radiation ($\lambda = 1.5405\text{\AA}$). The morphologies of PQDs were characterized with transmission electron microscopy (TECNAI G2F20, FEI). The fluorescence images of P-PQD microspheres were recorded by an inverted fluorescence microscope (Eclipse Ti-U, Nikon). The absolute fluorescence quantum yields of investigated fluorescence materials were tested by an absolute PL quantum yield spectrometer (Quantaaurus-QY C11347-01, Hamamatsu). The luminance of LED was measured by a spectroradiometer (SR-3A, Topcon).

Preparation of Cs-OA precursor: First, 0.814 g Cs_2CO_3 was mixed with 40 mL ODE and 2.5 mL OA followed by being dried at 120 °C for 1 h. Then Cs-OA was obtained after the above mixture reacted completely at 150 °C, which is evidenced by complete

dissolution of the Cs_2CO_3 . All above reactions were carried out with the protection of a N_2 atmosphere.

Synthesis of b-, g-, and r-PQDs: First, g-PQDs (CsPbBr_3) was synthesized by the methods developed by Protesescu,^{S1} with some modifications. Briefly, 5 mL ODE, 0.188 mmol PbBr_2 , 0.5 mL OA and 0.5 mL OAm were added into a reaction flask and heated at 120 °C for 1 h to remove water. Then the temperature of the mixture was raised up to 160 °C. After PbBr_2 dissolved completely, 0.4 mL of the Cs-OA solution pre-heated at 120 °C was injected into above reaction flask. All above reactions were carried out under a N_2 atmosphere. A few seconds later, the flask was quickly cooled down with an ice bath. The resultant solution was centrifuged at 10,000 rpm. The supernatant was discarded and precipitants (i.e. g-PQDs) were re-dispersed in hexane for further use. The b-PQDs ($\text{CsPb}(\text{Br}_{0.5}\text{Cl}_{0.5})_3$), and r-PQDs ($\text{CsPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$) were synthesized by very similar methods except that the mixture of PbBr_2 - PbCl_2 (0.094 mmol PbBr_2 + 0.094 mmol PbCl_2), and the mixture of PbBr_2 - PbI_2 (0.075 mmol PbBr_2 + 0.113 mmol PbI_2) were used instead of pure PbBr_2 (0.188 mmol), respectively.^{S2}

Synthesis of P-PQD composites: First, certain amount of solid paraffin was heated at 65°C until melt completely. Then, the PQD hexane solution was added into the melted paraffin with stirring, resulting in uniform PQD paraffin/hexane mixed solution. Finally, the P-PQD composites were obtained after the mixed solution was placed in vacuum drying oven at 65°C for 1 h to remove hexane.

Synthesis of P-PQD microsphere powder: P-PQD composites was added to spray bottle and temperature was raised up to 80°C. After melting completely, the composites was squirted out by pressing the spray bottle, forming solid microspheres

in the relatively cold air. The powder composed of P-PQD microspheres was collected and stored for further use.

Anion changes test: g-PQDs and r-PQDs hexane solutions were mixed with mass ratio of 1:1. Then, the fluorescence spectra of the mixed solution were measured at different time. Similarly, P-g-PQDs and P-r-PQDs powders were well mixed with mass ratio of 1:1 followed by measurement of fluorescence spectra at different time.

Fabrication of LEDs: P-b-PQDs, P-g-PQDs and P-r-PQDs powders were chosen to make blue, green and red LEDs, respectively. White light LEDs was prepared by using the mixture of P-b-PQDs, P-g-PQDs and P-r-PQDs powders in a certain ratio as the fluorescence layer. In the fabrication procedure, a small U-tube was filled with a certain amount of P-PQDs powder and inverted onto a UV LED chip (365 nm, jinyang optoelectronics, china) to make P-PQDs-absed LEDs.

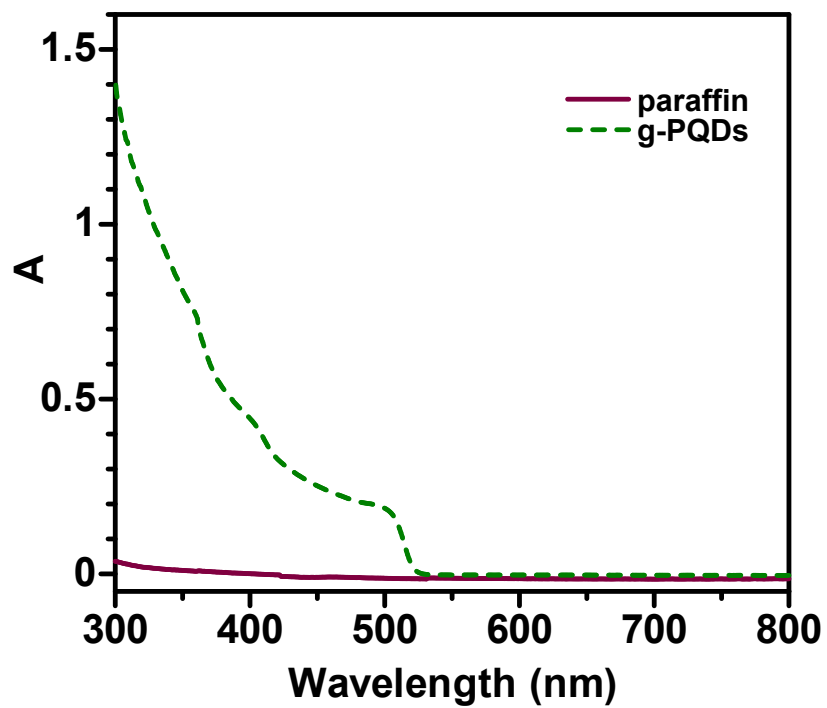


Figure S1. The UV-vis adsorption spectra of paraffin (10 mg/mL) in petroleum ether and g-PQDs (0.46 mg/mL) in hexane.

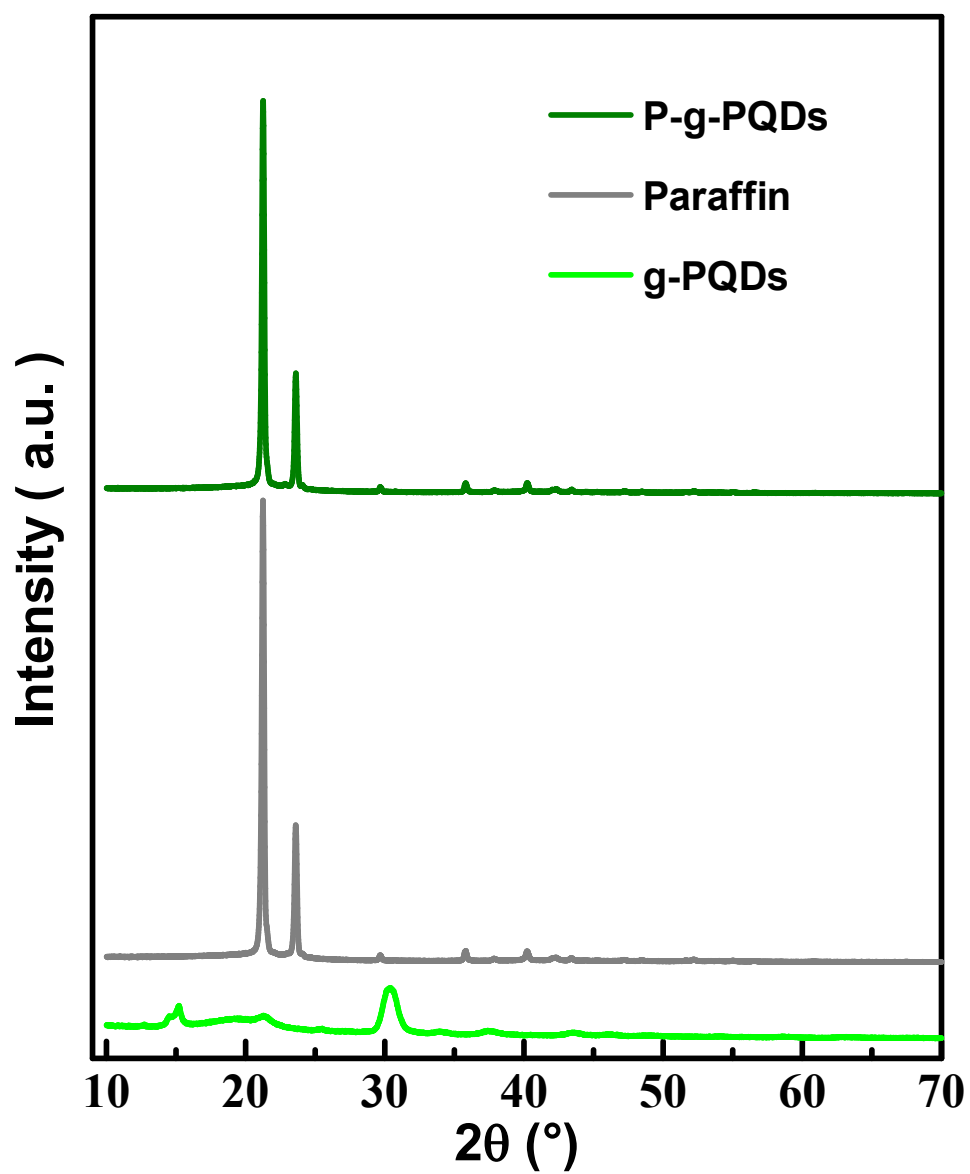


Figure S2. XRD patterns of g-PQDs, paraffin and P-g-PQDs .

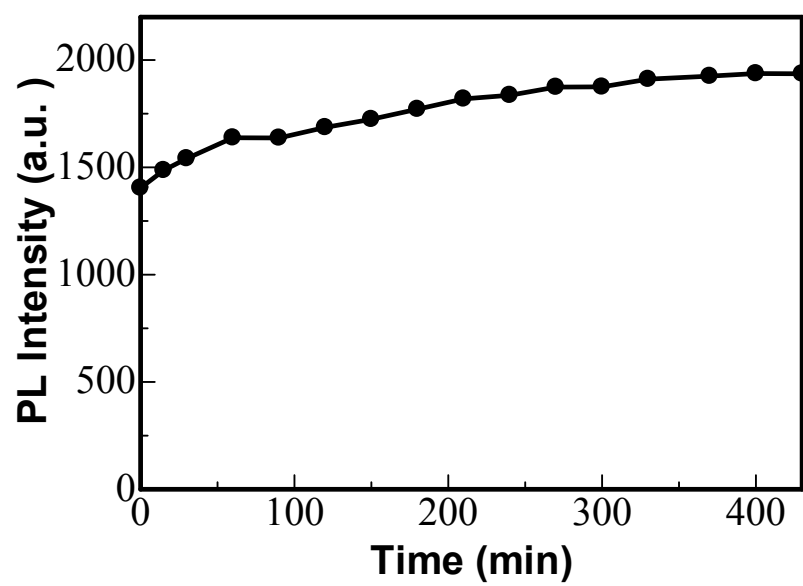


Figure S3. UV-stability investigated for P-g-PQDs.

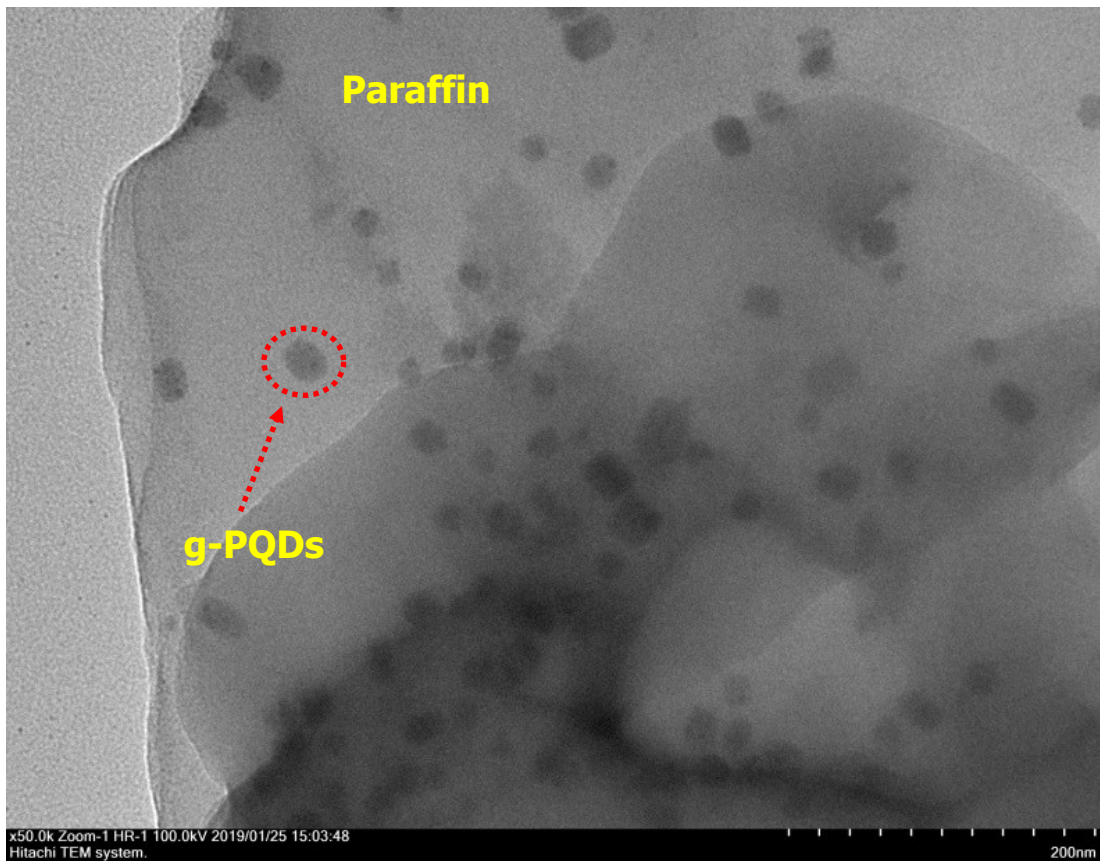


Figure S4. TEM image of P-g-PQD particles. The P-g-PQD microparticles were initially prepared by using higher melting point solid paraffin (Fischer-Tropsch wax with MP of 105°C), and then were further ground into smaller particles before TEM measurement.

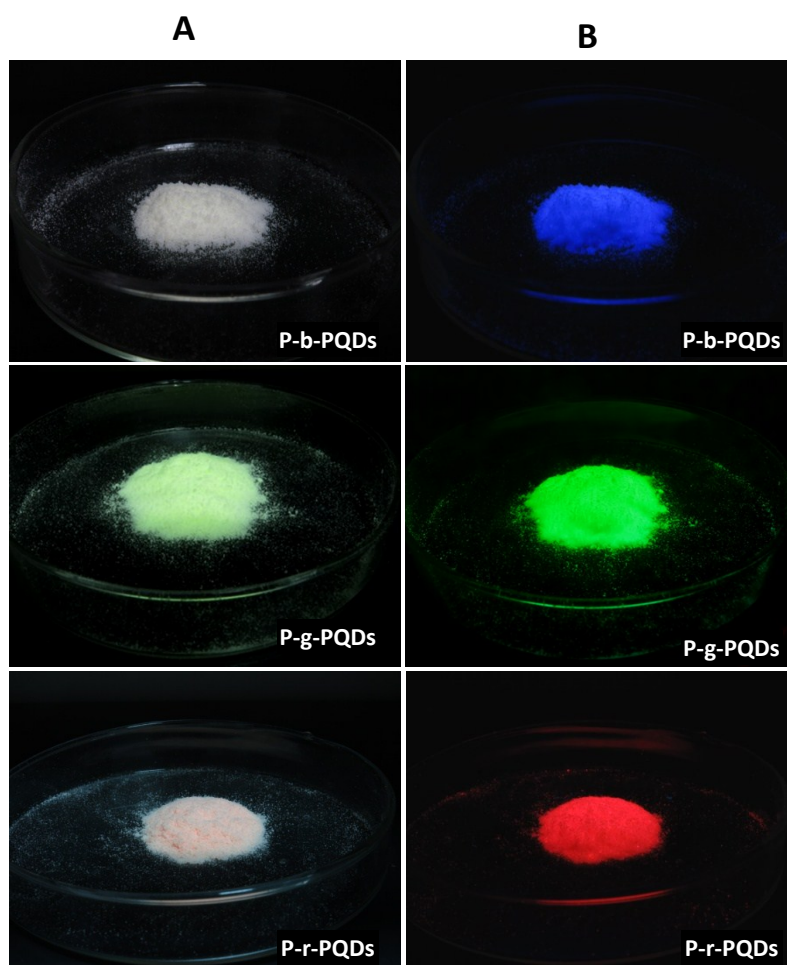


Figure S5. Photos obtained for P-b-PQD, P-g-PQD, and P-r-PQD microparticle powder under white light (A) and 365 nm UV light (B).

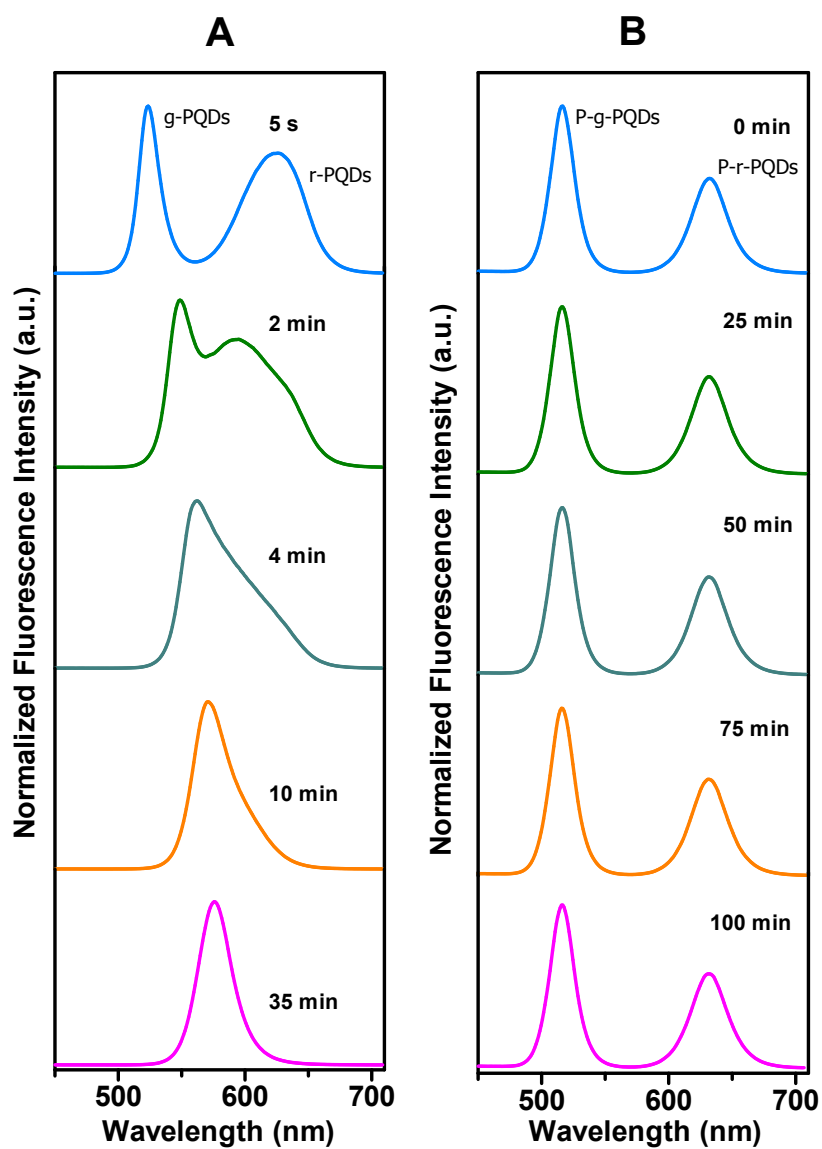


Figure S6. Anion exchanges investigated for PQDs : g-PQDs mixed with r-PQDs (A) ; and for P-PQDs: P-g-PQDs mixed with P-r-PQDs (B).

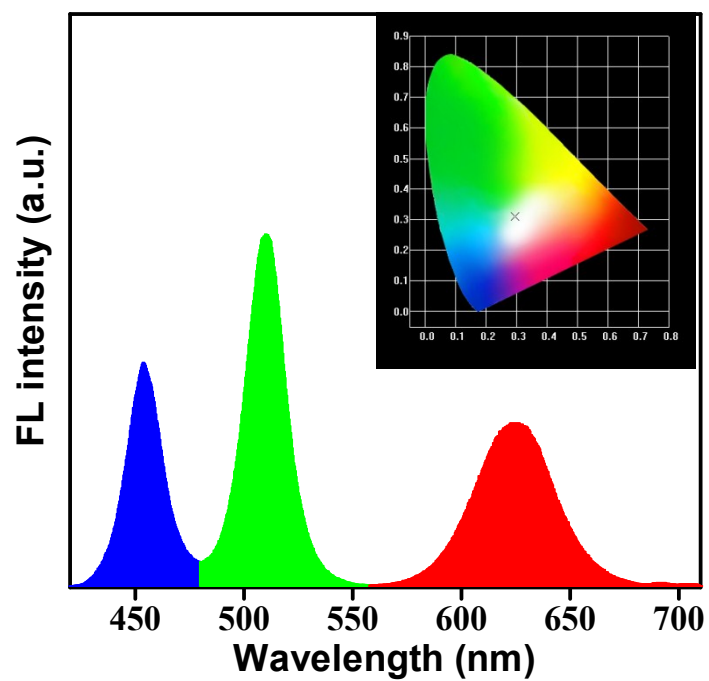


Figure S7. Emission fluorescence spectrum of a mixture of P-b-PQD, P-g-PQD and P-r-PQD microparticle powder under 365 nm UV light excitation. The inset spectrum reveals the color gamut of white light LED.

The measurements of the luminous efficacies of LEDs

The luminous efficacies of blue, green, red, and white LEDs (denoted as bLED, gLED, rLED, and wLED, respectively) were calculated from the measured luminances, according to following equation:^{S3}

$$\eta=4\pi LS/UI \quad (S1)$$

where η is luminous efficacy, L is the luminance, S is the area of LED coated with p-PQDs fluorescence powders, U is the voltage, and I is electric current. The experimental parameters, the measure luminances and the calculated η values for the LEDs listed in Table S1 .

Table S1. The measurements of the luminous efficacies of blue, green, red and white LEDs fabricated using P-b-PQDs, P-g-PQDs, P-r-PQDs and their mixture as the fluorescence powders, respectively.

LED type	LED area (m ²)	Luminance (cd/m ²)	Current (A)	Voltage (V)	Luminous efficacy (lm/W)
bLED	0.00022	1817	0.053	3.28	28.9
gLED	0.00022	5156	0.058	3.27	75.1
rLED	0.00022	2524	0.058	3.27	36.8
wLED	0.00022	2554	0.053	3.27	40.7

The measurement of junction temperature in the UV LED

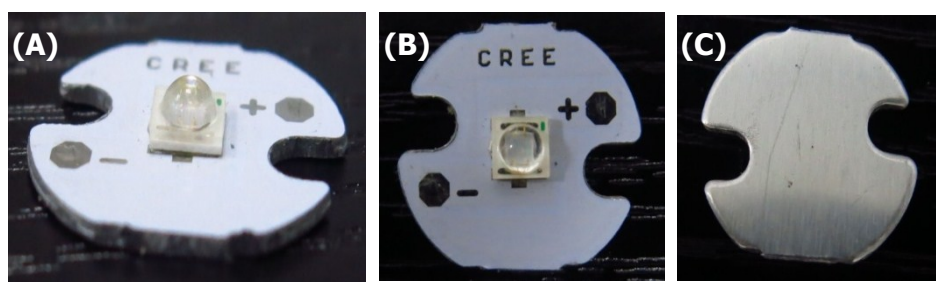


Figure S8. Photos of the UV LED chip with an aluminum heat sink used in the present work. (A) Side view; (B) top view ; and (C) back view.

The junction temperature of the UV LED used in the present studied (Table S2) was measured by a diode forward voltage method with following equations:^{S4,S5}

$$V_f = A + BT_o \quad (S2)$$

$$T_j = T_a + (V_f - V_a)/B \quad (S3)$$

Where V_a and V_f are initial and equilibrium forward voltages of the LED at certain current, T_o is the oven temperature, T_j and T_a are the junction and ambient temperatures, A and B are fitting parameters. By measuring the V_f value at each T_o under a small direct current of 0.5 mA (as listed in Table S2), and plotting the curve of V_f versus T_o (Figure S), the value of B was obtained to be -0.0017 mV/K.

Table S2. The equilibrium forward voltages of the LED at each oven temperature under a small dc current of 0.5 mA.

T_o (°C)	V_f (V)	B (mV/K)
40.9	2.820	
51.7	2.805	
61.1	2.788	-0.0017
72.0	2.768	
81.0	2.751	

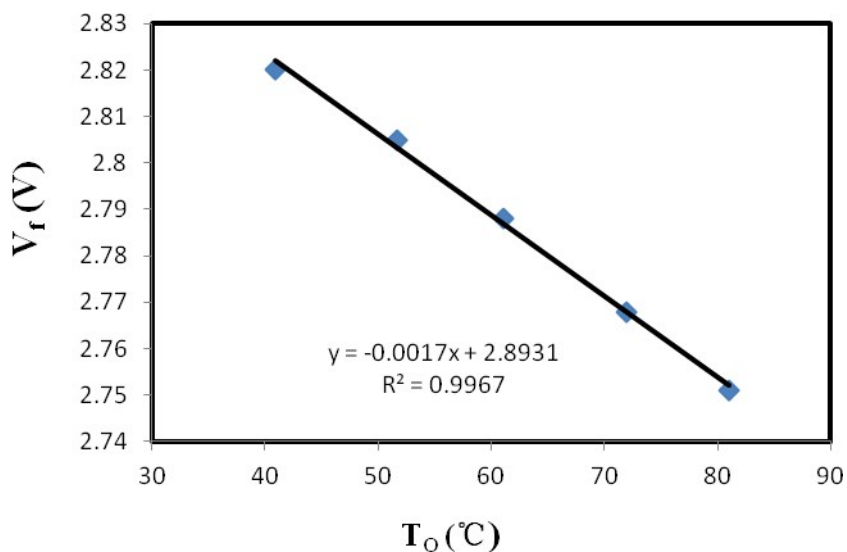


Figure S9. The plot of equilibrium forward voltage versus oven temperature under a small direct current of 0.5 mA.

The junction temperature (T_j) at normal working current of 50 mA was calculated by equation 2 and the measured data show in Table S3. The value of T_j at normal working current (50 mA) and ambient temperature of 28 °C was found to be 35.4°C.

Table S3. Calculation of junction temperature of the UV LED by the forward voltage method

Test No.	V_f (V)	V_a (V)	$V_f - V_a$ (V)	T_j (°C)	Average T_j (°C)
1	3.534	3.545	-0.011	34.5	35.4
2	3.531	3.544	-0.013	35.6	
3	3.531	3.545	-0.014	36.2	

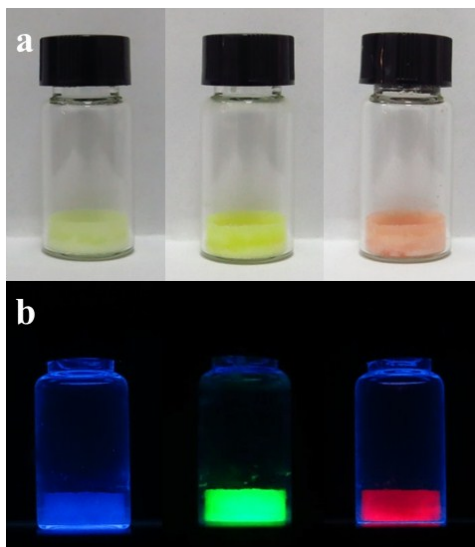


Figure S10. (a) White light and (b) 365 nm UV light photos of the high melt point of P-b-PQDs, P-g-PQDs, and P-r-PQDs.

References:

- S1 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. M. V. Walsh and Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.
- S2 H. Wang, S. Lin, A. Tang, B. P. Singh, H. Tong, C. Chen, Y. Lee, T. Tsai, R. Liu, *Angew. Chem. Int. Ed.* 2016, **55**, 7924 –7929.
- S3 S. R. Forrest, D.D.C. Bradley, M.E. Thompson, *Adv. Mater.*, 2003, **15**, 1043-1048.
- S4 A. Keppens, W. R. Ryckaert, G. Deconinck, P. Hanselaer, *J. Appl. Phys.*, 2008, **104**, 093104.
- S5 Y. Xi, E.F. Schubert, *Appl. Phys. Lett.*, 2004, **85**, 2163-2165.