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Emission Recovery and Stability Enhancement of Inorganic Perovskite Quantum Dots

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Abstract

Inorganic lead halide perovskite quantum dots (PQDs), especially red emission PQDs, are well-known to easily lose their luminescence emission with time, which shows from strong emission of fresh PQDs to no emission of aged PQDs. Here, we demonstrate that trioctylphosphine (TOP) can effectively and instantly recover the luminescence emission of aged red PQDs, making the “dead” PQDs “reborn”. Furthermore, TOP also works to improve the emission intensity of freshly synthesized PQDs. In this process, TOP does not make any detectable structural changes to PQDs. Besides, TOP can effectively enhance the stability of PQDs against long-term storage, temperature, UV irradiation, and polar solvents. This unusual emission recovery and stability enhancement by TOP shall promote the understanding of particle surface conditions and the development of PQD devices.

Graphical Abstract

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ASSOCIATED CONTENT

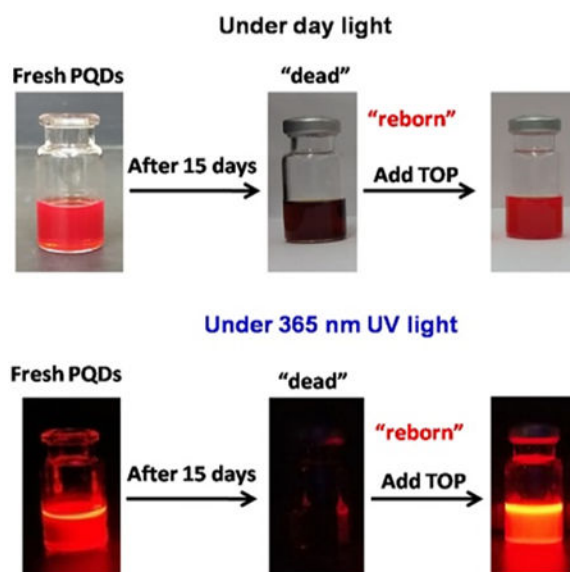
Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b01752.

Preparation process of perovskite quantum dots, additional TEM images, optical characterizations, pictures, NMR spectra, and XPS spectra (PDF)

Notes

The authors declare no competing financial interest.



Recently, all-inorganic perovskite quantum dots (PQDs) of cesium lead halide (CsPbX_3 , $\text{X} = \text{Cl, Br, I}$) have attracted increasing attention as a new class of fluorescent materials with a great potential for optoelectronic applications such as light-emitting diodes,^{1–5} photodetectors,^{6,7} single-dot spectroscopy,^{8–11} and lasers.^{12,13} PQDs have high photoluminescence quantum yields (PLQYs) and extremely narrow emission bands, and their emission can be easily tuned over the entire visible spectral region by controlling the composition and size¹⁴.

However, PQDs generally have poor stability against many ordinary factors, such as humidity, air, and temperature. A few methods have been proposed to enhance their stability. For example, PQDs could be embedded in organic polymer matrixes, poly(methyl methacrylate),¹⁵ or polystyrene,¹⁶ for good processability and stability. Zhang's group reported a silica coating of PQDs, and the coated PQDs (powder and gel) were stable in ambient for an extended time.^{17,18} All of those methods produced stable PQD block materials. Compared to the classical chalcogenide QDs, PQDs are more ionic in nature, and the ligands binding to the PQDs' surface are highly dynamic and labile.^{19,20} Even stored in solution under inert gas to avoid the influences from water vapor, and air, the PQD's photoluminescence still gradually decreases and finally is completely gone with time. Such aged PQDs without fluorescence are regarded useless for any optoelectronic applications. In a recent report,²¹ Alivisatos and colleagues used thiocyanate salts (NaSCN and NH_4SCN) to treat the aged CsPbBr_3 PQDs. This treatment improved the PLQY of the aged PQDs from 63 to 100%. This recovery presented an important advance to the understanding of the surface chemistry of PQDs. Besides, this treatment worked effectively on both of the freshly synthesized and the aged CsPbBr_3 PQDs. However, it did not exhibit any effect on $\text{CsPbBr}_x\text{I}_{3-x}$ PQDs.

We found that when trioctylphosphine (TOP) was added into the aged $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ PQD solution (lost most or all of its fluorescence emission) its fluorescence was instantly recovered. As shown in Figure 1a, a fresh PQD solution was red under daylight and had

strong red emission under 365 nm UV light. With time, the solution color gradually turned dark and the fluorescence emission decayed. After 15 days, the solution became brown and the fluorescence emission could not be visually seen under 365 nm UV light (aged PQDs). Nonetheless, when a little TOP was added into the aged PQD solution, the solution immediately turned back to red under daylight and exhibited strong red emission again under UV light. It is quite exciting to see the “dead” PQD’s instant rebirth. Even after the fresh PQDs were aged for more than 60 days in air, the emission still could be restored instantly with a little TOP. Detailed characterizations found that when TOP was introduced the emission wavelength red-shifted 7 nm and the fwhm narrowed from 46 to 36 nm compared to the aged PQDs (Figures 1b and S1). However, as shown in Figures 1c and S2, the absorption spectra had no obvious change. In Table 1, after 15 days, the PL intensity (aged) decreased to only 2.1% of its fresh state. When 20 μL of TOP was added into the aged PQD solution, the PL intensity was immediately back to 54.8% of the original intensity of its fresh state; with more TOP added, the PL intensity kept increasing and then leveled off at 110% of that of fresh PQDs when 80–120 μL TOP was added.

The effect of TOP on the fresh PQDs was also examined. When a different amount of TOP was added into the fresh PQD solution, the solution color became brighter under daylight and the fluorescence emission was stronger, a similar trend as the aged PQDs (Figures 2a, 2b). There was almost no change to the emission peak position with the addition of TOP (Figure 2c). The absorption spectra also did not change much (Figure 2d). Therefore, TOP only improved the PL intensity and retained the other optical properties for the fresh PQDs. The solid-state results were also observed and are shown in Figure S3. With the addition of TOP, the solid film of aged PQDs showed strong red emission again and the fresh PQDs film exhibited no obvious emission change.

To further investigate these phenomena, the PL lifetimes of the samples were measured. Time-resolved PL decays of aged PQDs, aged PQDs/TOP, fresh PQDs, and fresh PQDs/TOP are shown in Figure 3a. For aged PQDs, the average PL lifetime was 32.5 ns, and it became 51.9 ns for aged PQDs/TOP. The lifetimes were 41.5 and 61.8 ns for fresh PQDs and fresh PQDs/TOP. The instrument response function is shown in Figure S4. It was found that the lifetimes of PQDs after TOP treatment became longer than those before TOP treatment. It is well-known that surface defects have a great influence on the exciton lifetimes of quantum dots. Surface defects can be nonradiative surface states and then result in shorter exciton lifetimes.²² In many reports about PQD treatment, the PL lifetimes became longer after treatment, accompanied by increased PLQYs, which was attributed to the surface passivation.^{21,23,24} Therefore, in our work, the longer PL lifetimes indicated that TOP could effectively remove the surface defects and prevent the formation of nonradiative recombination pathways on the surface of PQDs, which led to enhancement of the PL intensity.

The long-term storage stability of PQDs, fresh PQDs/TOP, and aged PQDs/TOP was inspected. All of the samples were stored under N_2 protection. As shown in Figure 3b, the PL intensity of fresh PQDs decreased with time. Oppositely, the PL intensities of fresh and aged PQDs/TOP remained stable for 2 weeks. In fact, their PL intensities and emission peak

positions still showed no change after 6 weeks. It indicated that TOP could effectively enhance the optical and colloidal stability of PQDs in solution.

The thermal stability of fresh PQDs, fresh PQDs/TOP, and aged PQDs/TOP was also investigated (Figure 3c). Both of the PL intensities of the fresh PQDs and fresh PQDs/TOP decreased as the temperature rose. When the temperature reached 90 °C, the PL intensity of fresh PQDs/TOP decreased to 43% of the initial intensity, while it dropped to 16% for the fresh PQDs. When the temperature returned to room temperature, the PL intensity of fresh PQDs/TOP resumed to 93% of the initial intensity, while it was back to only 39% for fresh PQDs. The thermal circulation process was also performed, and no obvious intensity recession was observed (Figure S5). It indicated that TOP could effectively enhance the thermal stability of PQDs in solution.^{25–28} To further investigate the heat resistance of the TOP effect to PQDs, a harsher condition was applied. Sealed fresh PQDs and fresh PQDs/TOP toluene solutions were kept in boiling water for 30 min. As shown in Figures S6 and S7, the fresh PQDs lost fluorescence while the PQDs/TOP still exhibited strong red emission after this harsh heat process.

With constant irradiation under 365 nm UV light for 12 h, the PL intensity of fresh PQDs continuously decreased. However, the aged PQDs/TOP and fresh PQDs/TOP exhibited differently. The PL intensity of fresh PQDs/TOP first increased by 28% (this could be attributed to photoactivation) and then maintained (Figures 3d and S8). This indicated that TOP could effectively protect the PQDs from UV irradiation.

Besides the poor stabilities against temperature, UV irradiation, and long-term storage, PQDs are also sensitive to polar solvents and their high optical performance decreases because of their ionic nature,^{29–31} which further limits their applications. We found that the existence of TOP could also effectively improve the stability of PQDs with polar solvents. The PL behavior of fresh PQDs and fresh PQDs/TOP toluene solutions with different amounts of ethanol was monitored. As shown in Figure 3e, the PL intensity of the fresh PQDs decreased to 19.7% of the initial intensity when 40 μ L of ethanol was added; furthermore, the PL nearly disappeared after 400 μ L of ethanol was added. This expected emission decline can be clearly seen from the photos under daylight and UV light in Figure S9. However, the fresh PQDs/TOP exhibited very differently. The PL intensity had no change with 40 μ L of ethanol added (Figure 3f). When the ethanol amount was up to 400 μ L, the PL intensity still had no obvious change and the solution showed strong red emission (Figure S9). The PL intensity of the aged PQDs/TOP also exhibited better stability than fresh PQDs with the addition of ethanol (Figure S10). Therefore, TOP could effectively enhance the stability of PQDs with polar solvents.

In the molecular structure of TOP, phosphorus is the atom that may interact with the PQD particles. To further investigate this enhancement effect, two other phosphorus-containing molecules with similar molecular structures, tributylphosphine and triphenylphosphine, were tested. These two molecules both showed similar PL intensity enhancement to TOP for aged and fresh PQDs, but their long-term stabilities were both lower than that of TOP, and a precipitate was observed after 24 h with triphenylphosphine. The groups and the length of

the carbon chains attached to phosphorus have important influence on the PQD's colloidal stability, which was consistent with the literature.³²

The fresh PQDs and fresh PQDs/TOP solutions were centrifuged, and the obtained solid PQDs (precipitates) were directly used to for a few characterizations. TEM and X-ray diffraction (XRD) were performed to investigate the TOP effect. As shown in Figure 4a, the fresh PQDs were cubic with an average size of 14.5 ± 2.1 nm. The fresh PQDs/TOP also showed cubic shape, and the average size was 13.7 ± 1.7 nm. The HR-TEM images were obtained, and we found that the lattice spacing was the same with or without TOP treatment (Figure S11). It indicated that TOP did not make any obvious change to the morphology and particle size. The peak positions of the XRD spectrum of the fresh PQDs/TOP were the same as those of fresh PQDs (Figure 4b). Therefore, we believe that TOP did not make any structural changes to PQDs.

Furthermore, we also performed IR, ³¹P NMR, and XPS studies to further reveal what roles TOP played on the PQD surface. As shown in Figure 4c, the IR spectra of fresh PQDs and fresh PQDs/TOP were almost the same. We did not find the signatures related to TOP in fresh PQDs/TOP. ³¹P NMR analysis also confirmed no TOP bound to the aged or fresh PQD's surface after TOP treatment (Figure S12). When TOP was mixed with PQDs in hexane, its chemical shift was the same as that of pure TOP in hexane. After being centrifuged, the PQDs from the PQDs/TOP solution did not have the NMR signature of P. These results were different from other treated-PQD reports that the ligands were usually bound to the surface of PQDs.^{24,33,34} X-ray photoelectron spectroscopy (XPS) was carried out on the PQDs from the PQDs/TOP solution, and there was no P signature found, which could further support the IR and ³¹P NMR results (Figure S13). The XPS analysis also revealed no significant changes in element compositions (Cs, Pb, Br, and I) of the PQDs with or without TOP treatment. The ratios of Pb:(Br+I) were the same for the aged and fresh PQDs with or without TOP treatment. Additionally, the high-resolution spectra of the Pb 4f_{7/2} and Pb 4f_{5/2} also exhibited no change (Figure 4d).

Generally, inorganic lead halide perovskite materials are regarded with high defect tolerance, which may come from their ionic nature or the orbital composition of the energy bands.^{35,36} However, quite a few publications argued the influence of surface defects on the PL multicomponent decay kinetics of PQDs.^{10,14,15} In Alivisatos's work,²¹ the PLQY improvement after treatment was attributed to the removal of excess lead from the surface of CsPbBr₃ PQDs. TOP was also reported to remove the excess Se on the surface of CdSe QDs and made the QDs activated.³⁷ However, there were no significant changes in element compositions (Cs, Pb, Br, and I) of the PQDs with or without TOP treatment in our work. TOP can be used as both a surfactant and a solvent for nanoparticle synthesis. It can dissolve the precursors and control the size, morphology, and stability of the nanoparticles.^{38–42} On the basis of these facts, we rationalize that in our case TOP effectively promoted some ions to migrate on the PQD surface to repair existing surface defects for better emissions.²¹ This ion migration should also increase the various stabilities of PQDs when they have perfect surface conditions. Considering the very fast interparticle halogen ion exchanges among CsPbBr₃ and CsPbI₃ PQD particles in solution,^{43–45} our assumption for quick ion migration on the particle surface is reasonable.

Finally, we tested the TOP-treated PQDs for light-emitting devices (LEDs). A blue light emission chip (460 nm) was used to prepare PQD LEDs. The LEDs showed strong red emission with a peak wavelength of 640 nm and a fwhm of 30 nm, as shown in Figure 5a. The CIE color coordinates of the LEDs were (0.6948, 0.2965) (Figure 5b). The luminance of the LEDs was measured against the working time. As shown in Figure 5c, the LED's luminance from untreated PQDs continuously decreased with time. After the LED worked 150 min, its luminance reduced to 52% of its original value (104 versus 200 $\text{cd}\cdot\text{m}^{-2}$). However, the PQDs/TOP LED exhibited no change in 150 min. Therefore, the LEDs based on TOP-treated PQDs exhibited great stability. Furthermore, the maximum luminance of TOP-treated PQD LEDs reached 2321 $\text{cd}\cdot\text{m}^{-2}$ under an applied current of 750 mA (the voltage was 3.3 V).

Wu et al. used TOP oxide in the synthesis and found increased PQD stability against ethanol.⁴⁶ In Geyer's recent work, they used TOP as part of the postsynthesis treatment on CsPbI_3 PQDs and found that the quantum yield remained at 30% after 1 month.⁴⁷ We reported a unique case that very little TOP instantly brought "dead" PQDs alive. This is very unusual, and it indicates that the fluorescence loss with time is probably not due to the generally accepted degradation mechanism; otherwise, the recovery could not be instant. This phenomenon points out a different way (backward, i.e., recovery) to understand the surface condition and emission mechanism of PQDs. In addition to improving the fluorescence strength of freshly made already bright PQDs, TOP significantly enhances multiple stabilities of PQDs against long-term storage, temperature, UV irradiation, polar solvents, and the lifetime of the LEDs made from them. We found that this effect (from TOP, tributylphosphine, and triphenylphosphine) also worked on CsPbBr_3 and CsPbI_3 PQDs. Another important difference from existing reports is that we did not find any P signal in isolated PQD samples; this probably explains why just very little TOP can work. This unusual emission recovery and stability enhancement by TOP shall promote understanding of the particle surface condition and the development of PQD devices.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

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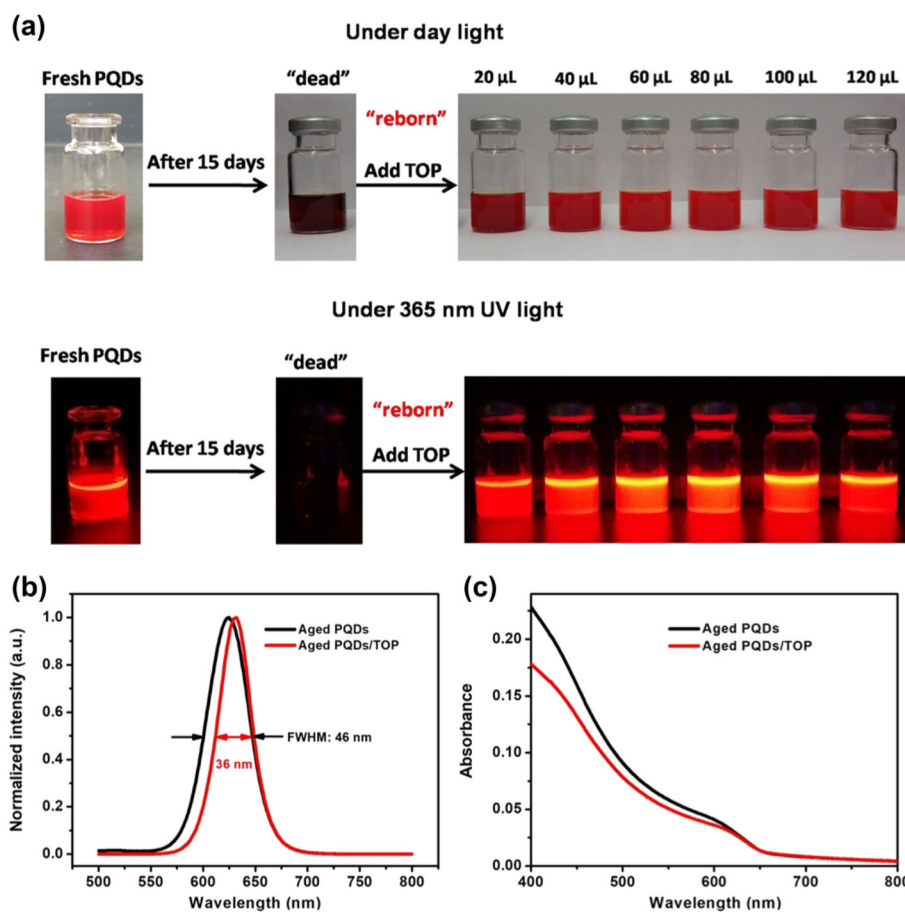


Figure 1.

(a) Photos of fresh/aged PQDs and aged PQDs with different amounts of TOP under daylight (top) and UV light (bottom). (b) Normalized PL spectra of aged PQDs with and without TOP (80 μL of TOP added to 5 mL of PQD solution). (c) Absorption spectra of aged PQDs with and without TOP (80 μL of TOP added to 5 mL of PQD solution).

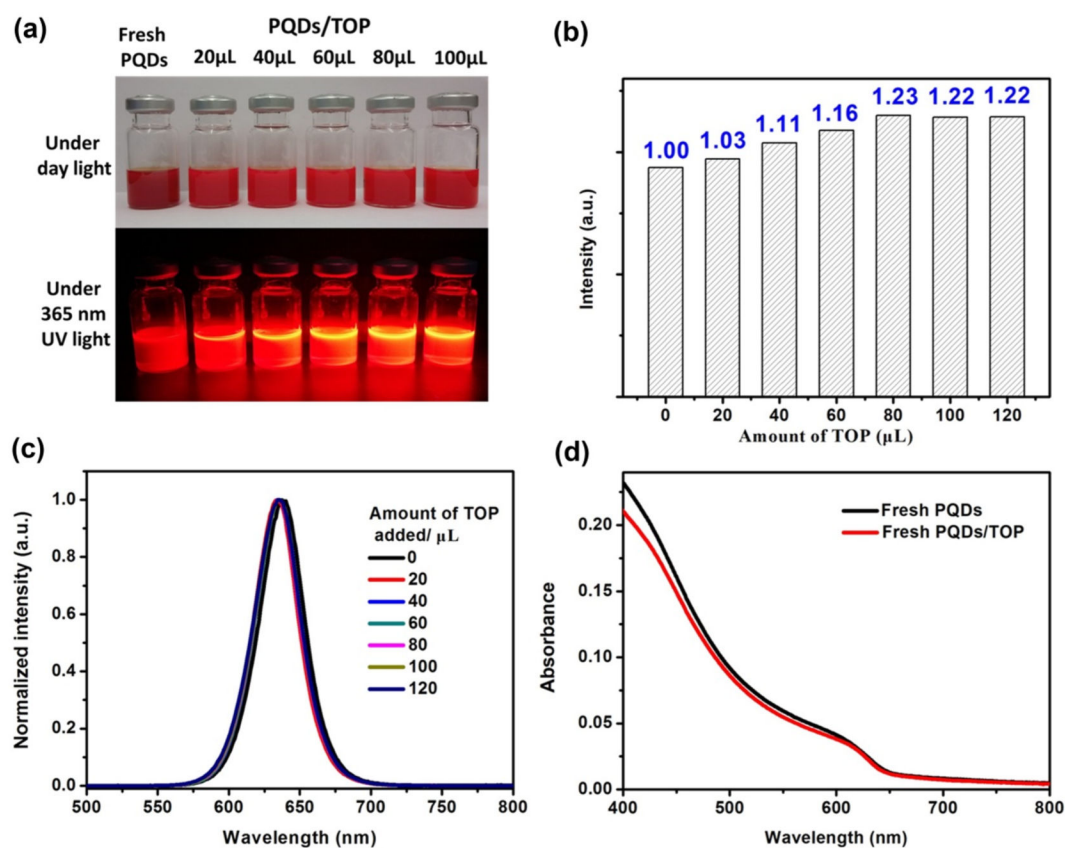
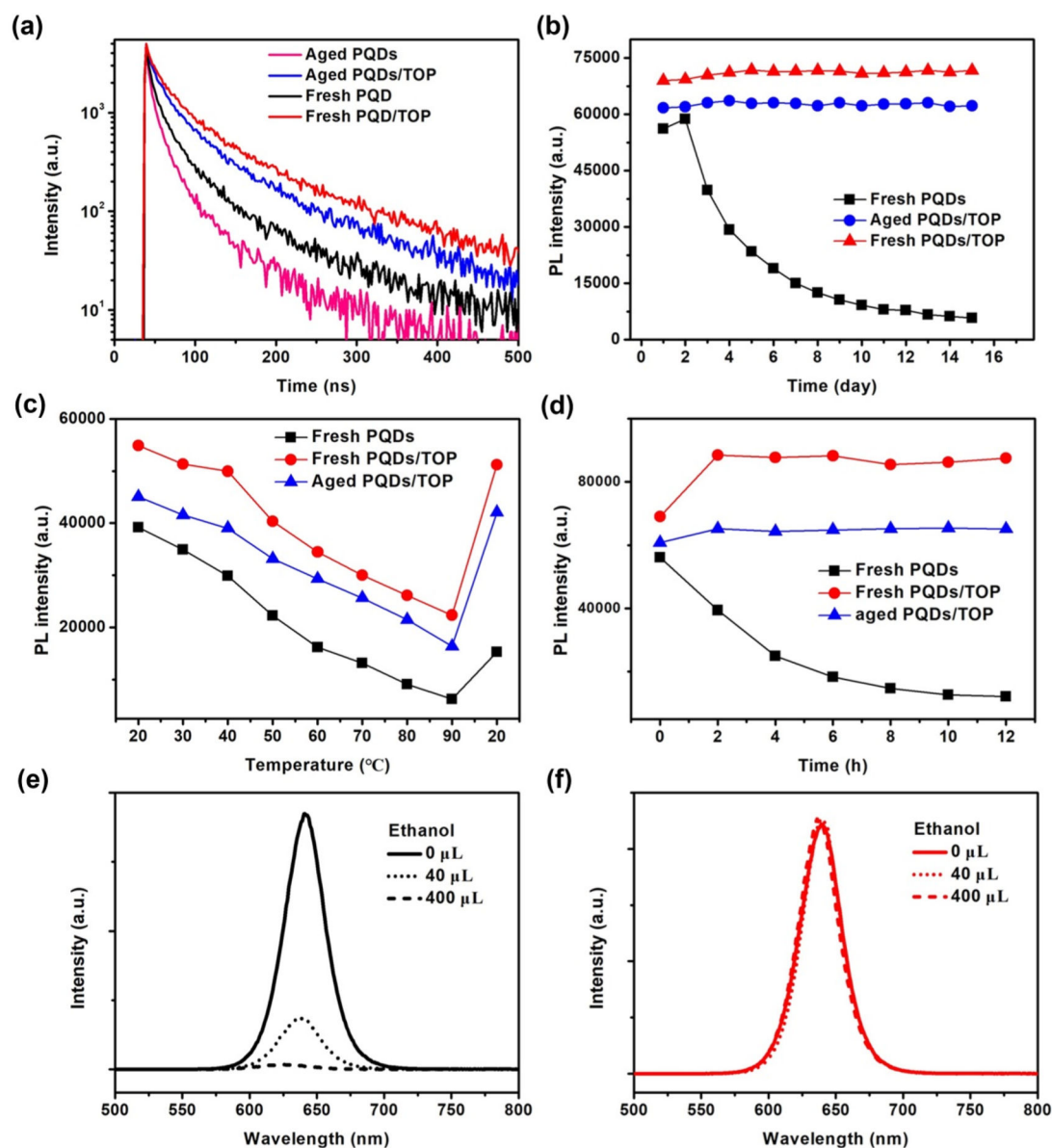


Figure 2.

(a) Photos of fresh PQDs with different amounts of TOP under daylight (top) and UV light (bottom). (b) Relative PL intensities and (c) spectra of fresh PQDs with TOP. (d) Absorption spectra of fresh PQDs and fresh PQDs/TOP (80 μL of TOP).

**Figure 3.**

(a) Time-resolved PL lifetimes of fresh PQRs, fresh PQRs/TOP, aged PQRs, and aged PQRs/TOP. (b) PL stability of fresh PQRs, fresh PQRs/TOP, and aged PQRs/TOP against storage time. (c) Thermal and (d) UV irradiation stabilities of fresh PQRs and fresh PQRs/TOP. PL spectra of fresh PQRs (e) and fresh PQRs/TOP (f) toluene solutions with different amounts of ethanol added.

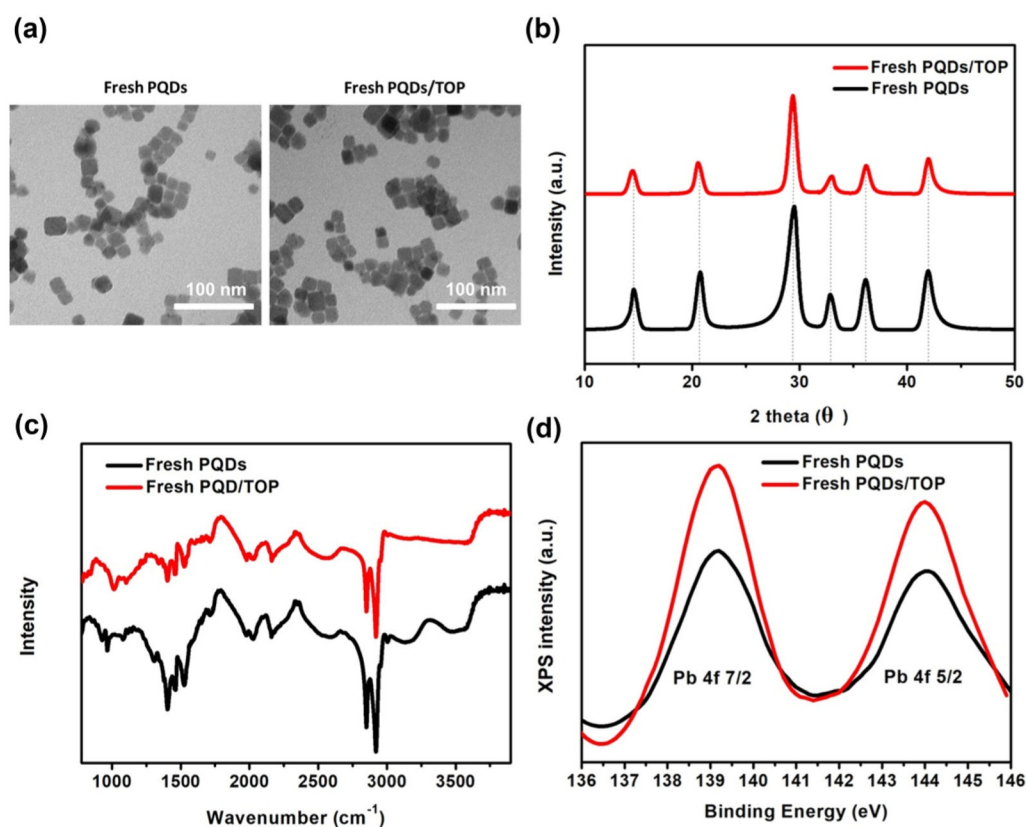


Figure 4.

TEM images (a), XRD spectra (b), IR spectra, (c) and XPS spectra of the Pb 4f (d) of the fresh PQDs and fresh PQDs/TOP.

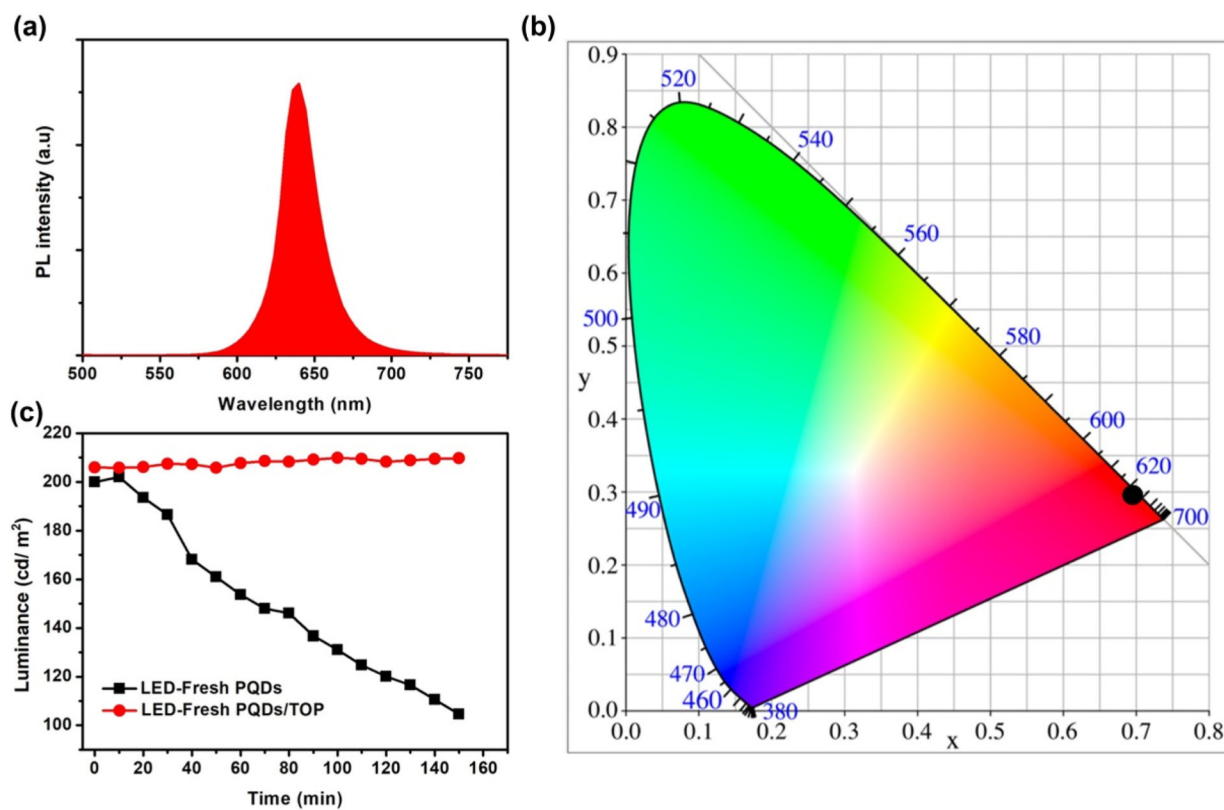


Figure 5.

(a) PL spectrum and (b) CIE color coordinates of the LEDs. (c) LED luminance against the working time.

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Table 1.

Relative PL Intensities of Fresh/Aged PQDs and Aged PQDs with TOP

PQDs	aged PQDs with TOP (μL)							
	fresh PQDs	aged PQDs	20	40	60	80	100	120
relative PL intensity	1.00	0.021	0.548	0.790	1.04	1.10	1.07	1.08