

## Electronic Supporting Information

### **Ultra-stable water-dispersive perovskite QDs encapsulated by triple siloxane coupling agent system with different hydrophilic/hydrophobic properties**

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## EXPERIMENTAL

**Materials and chemicals** NH<sub>2</sub>-PEG was synthesized according to a previous literature.<sup>[1]</sup> (3-Triethoxysilyl) propyl isocyanate (ICPTES) (97%) and (3-aminopropyl) triethoxysilane (APTES) (99%) were purchased from Sinopharm. Perfluorooctyltrimethoxysilane (PFMS) was provided by Alfa Aesar chemical co. ltd. Ditiin butyl dilaurate (DBTDL), PbBr<sub>2</sub> (99%), CsBr (99.9%), p-toluenesulfonyl chloride (p-TsCl), ethylenediamine, triethylamine, and hydrobromic acid (HBr) (48% in water) were purchased from Aladdin Reagent Co., Ltd. Poly(ethylene glycol) (mPEG<sub>113</sub>) was obtained from Shanghai Yuanye Biological Technology Co., Ltd. Toluene, N,N-dimethylformamide (DMF), dichloromethane (DCM), methanol, ethanol, tetrahydrofuran (THF), and acetone were obtained from Beijing Chemical Works.

**Synthesis of silane coupling agent modified by polyethylene glycol (Si-PEG)** Into a round-bottom flask were added catalyst amount DBTDL, mPEG<sub>113</sub> (5.0 g, 1.0 mmol), and 20 mL of anhydrous tetrahydrofuran (THF). After slowly dropwise of 0.24 mL ICPTES, the reaction was kept for the stir at room temperature for one day (molar proportion of ICPTES and mPEG<sub>113</sub> is 1:1). The reaction mixture was precipitated in cold ethyl ether three times, and the resulted product was vacuum-dried.

**Synthesis of PQDs@SiO<sub>2</sub>-a** PQDs@SiO<sub>2</sub>-a was synthesized by using the LARP method as described below. Briefly, PbBr<sub>2</sub> (0.4 mmol, 0.146 g), CsBr (0.2 mmol, 0.042 g), and APTES (100 μL) were mixed in 10 mL DMF, and then 20 μL of HBr was injected into the above solution. The above solution was uniformly mixed quickly as the precursor. Under vigorous stirring, 500 μL of the precursor was added to 10 mL toluene rapidly. The mixture solution immediately showed strong fluorescence emission. After stirring for 20 min to complete the reaction, the toluene solution was centrifuged at 10000 rpm for 5 min, and a precipitate with bright fluorescence was obtained.

**Synthesis of PQDs@SiO<sub>2</sub>-b** PQDs@SiO<sub>2</sub>-b was synthesized by the LARP method. Briefly, PbBr<sub>2</sub> (0.4 mmol, 0.146 g), CsBr (0.2 mmol, 0.042 g), APTES (100 μL), and PMFS (250 μL) were mixed in 10 mL DMF, and then 20 μL of HBr was injected into the above solution and then 20 μL of HBr was injected into the above solution. The above solution was uniformly mixed quickly as the precursor. Under vigorous stirring, 500 μL of the precursor was added to 10 mL toluene rapidly. The mixture solution immediately showed strong fluorescence emission. After stirring for 20 min to complete the reaction, the toluene solution was centrifuged at 10000 rpm for 5 min, and a precipitate with bright fluorescence was obtained.

**Synthesis of PQDs@SiO<sub>2</sub>-c** The synthesis of PQDs@SiO<sub>2</sub>-c was similar to that of PQDs@SiO<sub>2</sub>-b, except adding 5 mg NH<sub>2</sub>-PEG in the toluene during the synthetic process.

**Synthesis of PQDs@SiO<sub>2</sub>-d** The synthetic procedure of PQDs@SiO<sub>2</sub>-d was similar to that of PQDs@SiO<sub>2</sub>-b, except adding 15 mg Si-PEG in the toluene during the preparation process.

**Cytotoxicity evaluation and cellular imaging** HeLa cells were selected to the cytotoxicity evaluation and cellular imaging and were cultured in Dulbecco's modified Eagle's medium (DMEM) with fetal bovineserum (10%) (37 °C and 5% CO<sub>2</sub>). The cytotoxicity evaluation of PQDs@SiO<sub>2</sub>-d was proved by the methylthiazolyldiphenyltetrazolium bromide (MTT) assays. After 24h of incubation of HeLa cells in a 96-well plate, a fresh cell culture media with different concentrations of PQDs@SiO<sub>2</sub>-d (20–120 μg mL<sup>-1</sup>) was used to replace the old one and further cultured for 24 h. After 20h incubation, adding 15 μL DDB to each well was incubated for 4 h. Finally, using a Tecan Infinite M1000 plate reader (Durham, NC, USA) determined the OD value of each well under the wavelength at 490 nm.

For cell imaging, HeLa cells were incubated on 8-well chamber (37 °C and 5% CO<sub>2</sub>) for 24 h firstly, and then fresh medium containing PQDs@SiO<sub>2</sub>-d (20 μg mL<sup>-1</sup>) was used to replace the old one. After 4 h incubation, the obtained HeLa cells were washed with PBS, and 4',6-

diamidino-2-phenylindole (DAPI) was added to 10 min prior to the imaging for nuclear counterstaining. Prior to imaging, cells were washed with PBS for three times. After washing, the cell imaging as performed on a confocal laser scanning microscope (Nikon C1Si).

**Characterization** TEM images were measured on JEOL-2100F electron microscope. All PL spectra, PLQYs, and PL lifetimes were recorded with a fluorescence spectrophotometer (Edinburgh FLSP920). UV–vis absorption spectra were performed on a UV–vis spectrophotometer (SHIMADZU UV-2550). FTIR spectra were performed with a FTIR spectrometer (Magna 560). XRD measurements were recorded using a Rigaku D/max-TTR-III diffractometer using Cu Ka radiation ( $\lambda=0.15405$  nm). XPS spectra were performed with a VGESCALAB 220-IXL spectrometer.

**Exponential fitting of PL decays and calculation** Decay time of the samples was obtained from the decay curves, which is simulated by using a biexponential decay function (1):

$$I(t) = A_0 + A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2) \quad (1)$$

where  $I(t)$  is the PL intensity at time  $t$ ,  $A_i$  are the weight constants,  $\tau_1$  and  $\tau_2$  represent the PL decay time. The mean lifetime  $\tau_{ave}$  is calculated by the formula (2):

$$\tau_{ave} = \frac{A\tau_1^2 + B\tau_2^2}{A\tau_1 + B\tau_2} \quad (2)$$

where  $\tau_1$  and  $\tau_2$  are the PL decay time, and  $A$  and  $B$  represent the ratio of component contribution to the decay. Actually,  $\tau_1$  is due to an internal reorganization, while  $\tau_2$  is from the surface state reorganization. The radiative lifetime ( $\tau_r$ ) and non-radiative lifetime ( $\tau_{nr}$ ) can be calculated by the following formula:

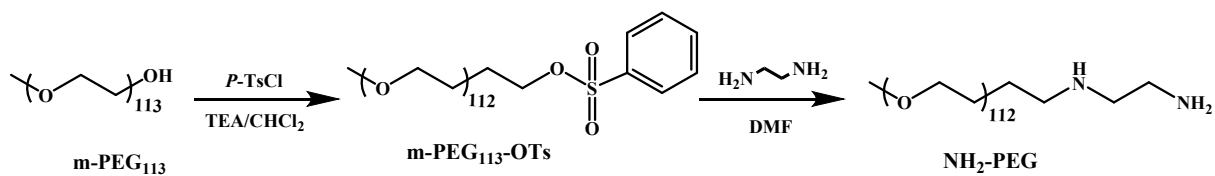
$$\tau_{ave} = \frac{1}{k_f + \sum k_i} \quad (3)$$

$$PLQY = \frac{k_f}{k_f + \sum k_i} \quad (4)$$

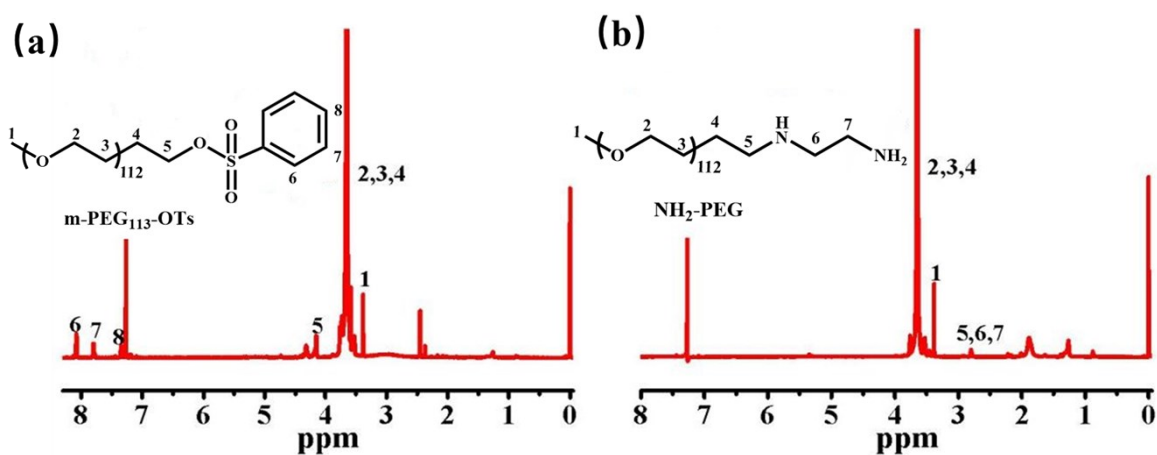
$$\tau_r = \frac{1}{k_f} \quad (5)$$

$$\tau_{nr} = \frac{1}{\Sigma k_i} \quad (6)$$

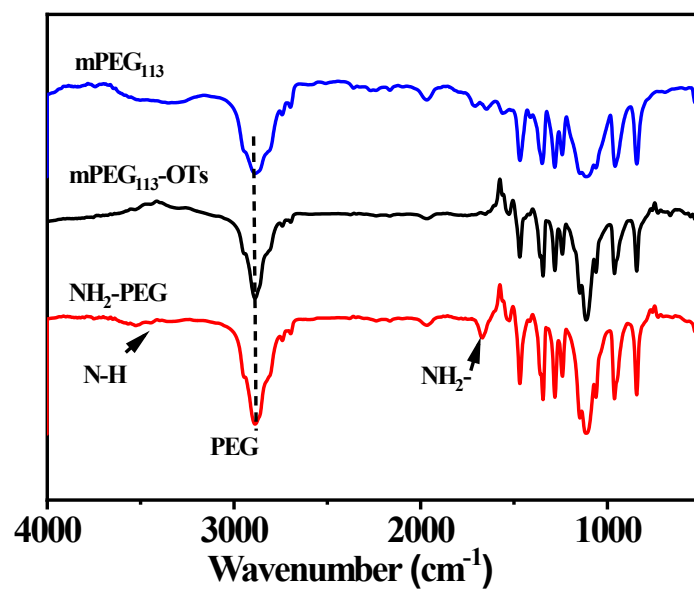
where  $k_f$  and  $\Sigma k_i$  represent the radiative recombination and non-radiative recombination rate constant, respectively.



**Scheme S1.** Synthetic route of NH<sub>2</sub>-PEG.



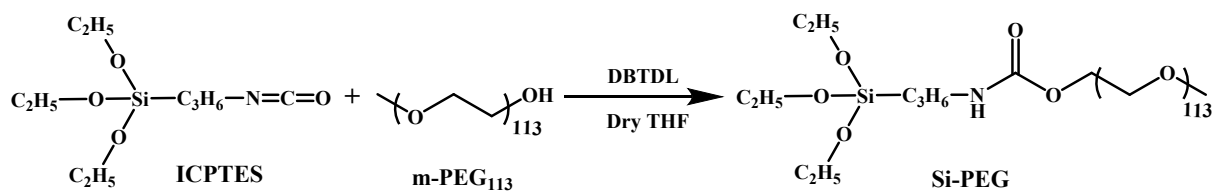
**Fig. S1.** <sup>1</sup>H-NMR spectra for a) mPEG<sub>113</sub>-OTs and b) NH<sub>2</sub>-PEG.



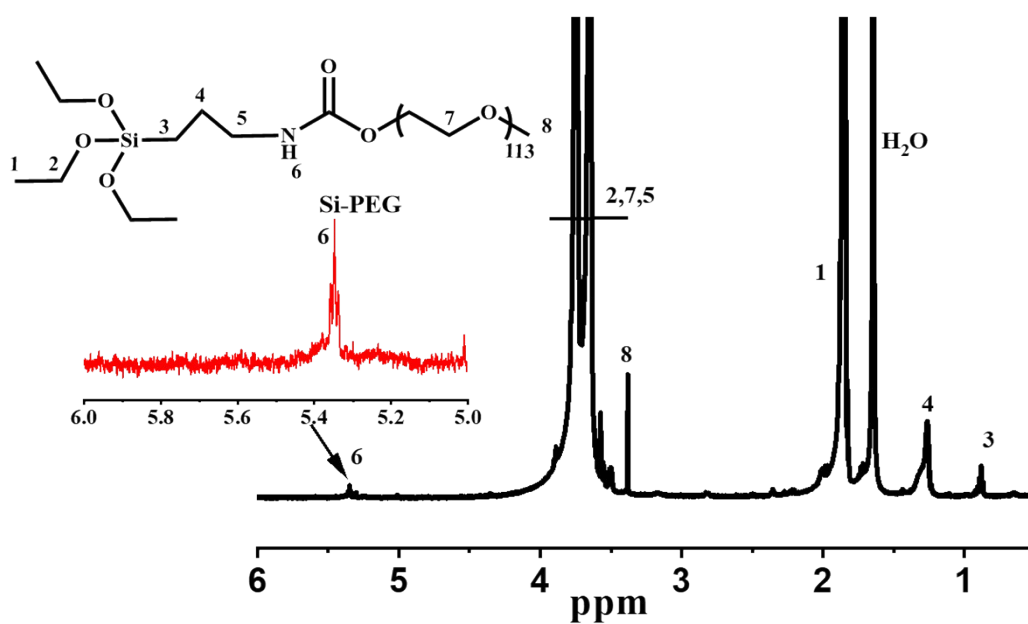
**Fig. S2.** FTIR spectra for mPEG<sub>113</sub>, mPEG<sub>113</sub>-OTs, and NH<sub>2</sub>-PEG.

As shown in Scheme S1, the NH<sub>2</sub>-PEG was synthesized by the reaction of ethylenediamine with active intermediate mPEG<sub>113</sub>-OTs obtained from m-PEG<sub>113</sub> and p-toluenesulfonyl chloride (p-TsCl). The chemical structure of NH<sub>2</sub>-PEG was confirmed by <sup>1</sup>H NMR and FTIR (Fig. S1 and S2). The signal 1 at 3.39 ppm can be attributed to the terminal methoxy of mPEG<sub>113</sub> and the broad signal at 3.5-4.0 ppm is assigned to the methylene hydrogen of the PEG main chain (Fig. S1a). The peak at 4.17 ppm is ascribed to the methylene hydrogen which connected to p-toluenesulfonate. The signals at 7.0-8.3 ppm are characteristic peaks of the benzene ring in p-toluenesulfonate. In Fig. S1b, the broad signals at 3.0-3.5 ppm are assigned to methylene which connected to the amino group and the signals corresponding to the p-toluenesulfonate group disappeared. From the FTIR spectra (Fig. S2) of m-PEG<sub>113</sub>-OTs and NH<sub>2</sub>-PEG, the characteristic peak of N-H at 1680 cm<sup>-1</sup> also can be observed, which indicates that -OTs group has been replaced by ethylenediamine to obtain the target product NH<sub>2</sub>-PEG.

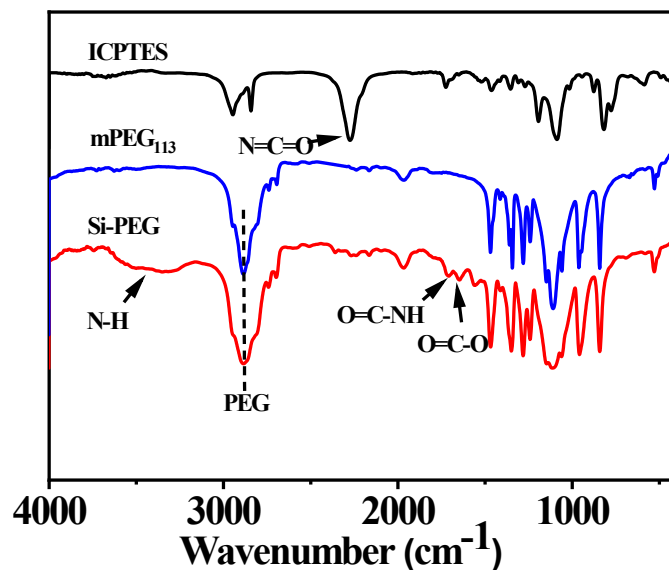




**Scheme S2.** Synthetic route of Si-PEG.

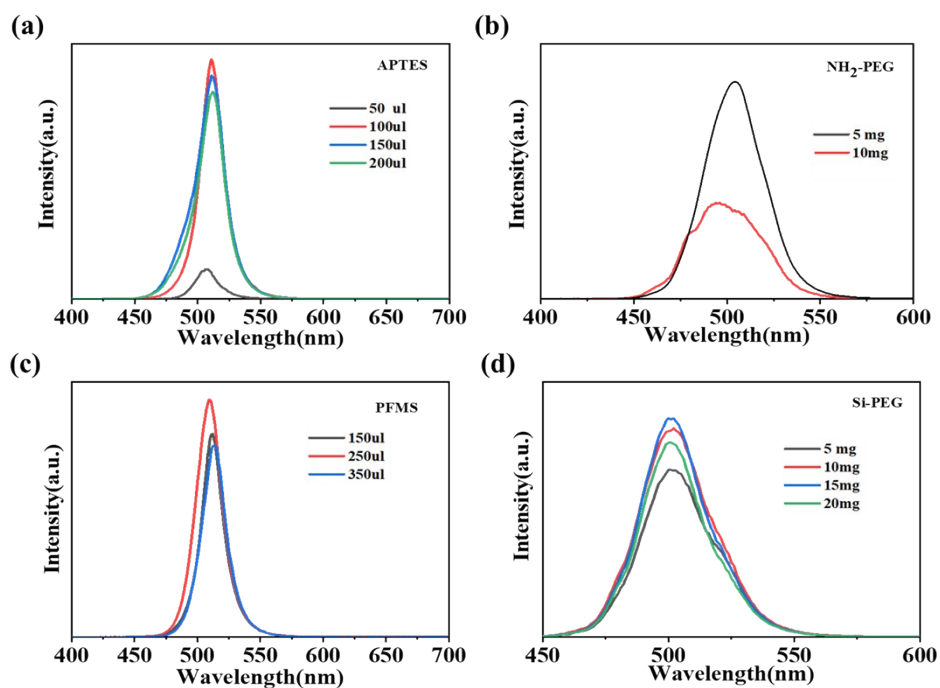


**Fig. S3.** <sup>1</sup>H-NMR spectra for Si-PEG.

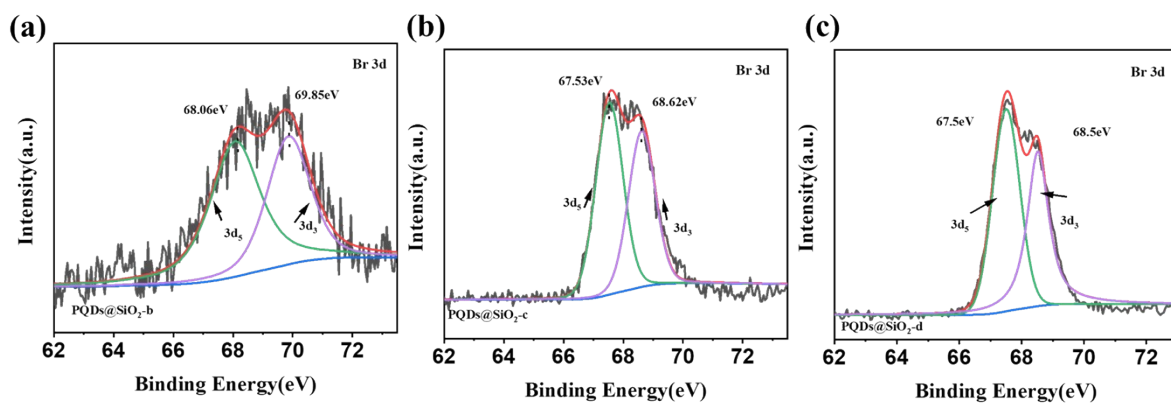


**Fig. S4.** FTIR spectra for ICPTES, mPEG<sub>113</sub>, and Si-PEG.

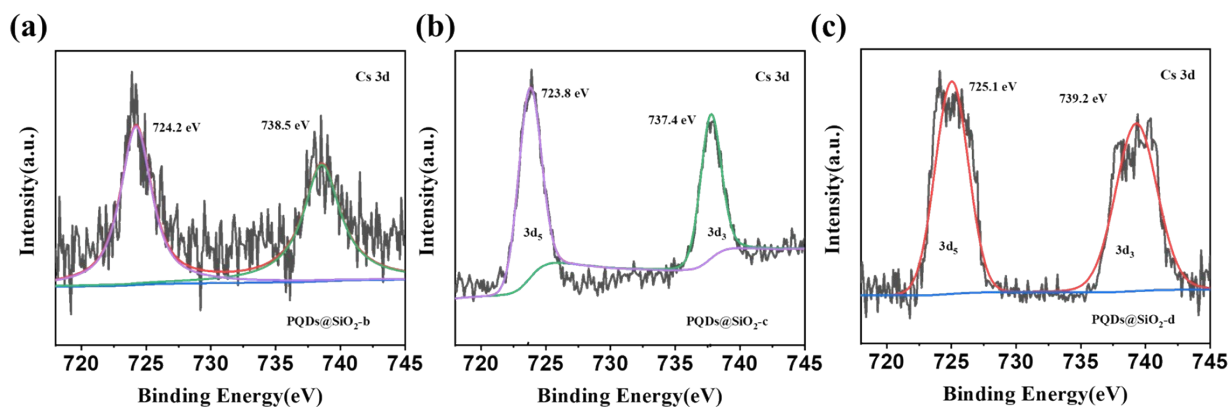
The Si-PEG was prepared by the polyaddition reaction between the isocyanate group (3-triethoxysilyl) propyl isocyanate (ICPTES) and the hydroxyl group on the end of m-PEG<sub>113</sub> (Scheme S2). The peak at 5.3-5.4 ppm can be attributed to the newly formed N-H group by polyaddition reaction (Fig. S3). As shown in Fig. S3, the characteristic signal at 3.39 ppm can be attributed to the methylene of m-PEG<sub>113</sub>. The peaks at 0.78-0.83, 1.38 ppm are assigned to the methylene in ICPTES. The broad peak at 1.8-2.0 ppm is attributed to the methyl in ICPTES. From the FTIR spectra (Fig. S4), the characteristic peak of -N=C=O at 2273 cm<sup>-1</sup> disappeared and a new peak corresponding to the urethane group was observed at 1760-1530 cm<sup>-1</sup>. The above results indicated the successful synthesis of Si-PEG.



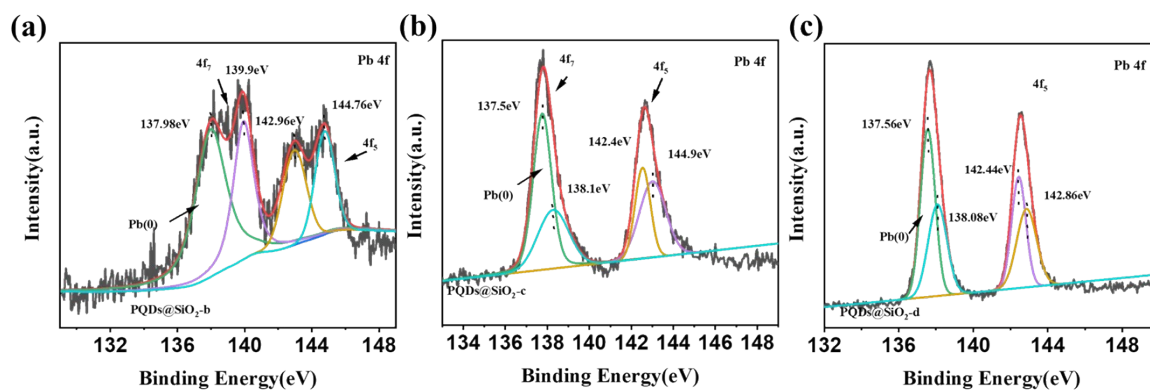
**Fig. S5.** (a) PL spectra of PQD's colloidal solutions obtained by different feeding amount of APTES with 20  $\mu$ L of HBr. (b) PL spectra of PQD's colloidal solutions obtained by different concentrations of PFMS with 100  $\mu$ L of APTES and 20  $\mu$ L of HBr. (c) PL spectra of PQD's colloidal solutions obtained by different concentrations of NH<sub>2</sub>-PEG with 100  $\mu$ L of APTES, 20  $\mu$ L of HBr, and 250  $\mu$ L of PFMS. (d) PL spectra of PQD's colloidal solutions obtained by different concentrations of Si-PEG with 100  $\mu$ L of APTES, 20  $\mu$ L of HBr, and 250  $\mu$ L of PFMS.



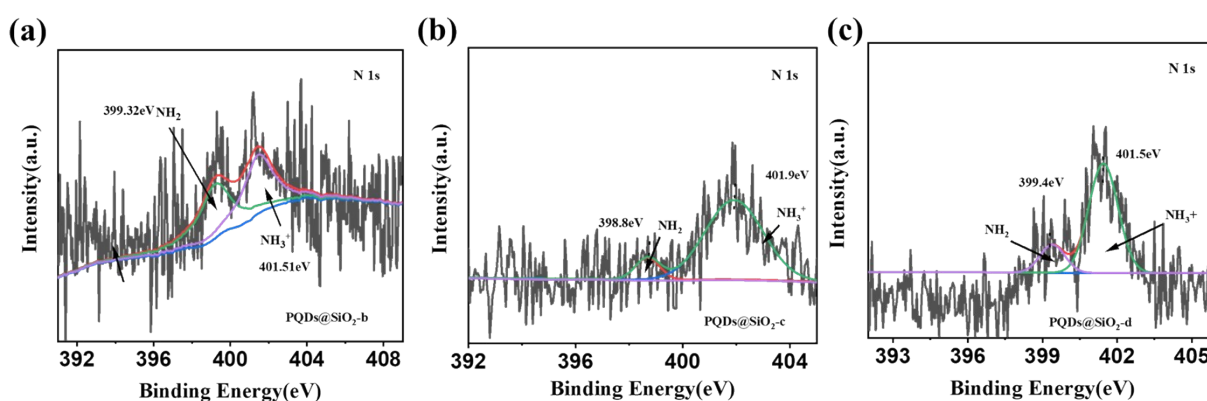
**Fig. S6.** High-resolution Br 3d spectra of (a) PQDs@SiO<sub>2</sub>-b, (b) PQDs@SiO<sub>2</sub>-c, and (c) PQDs@SiO<sub>2</sub>-d.



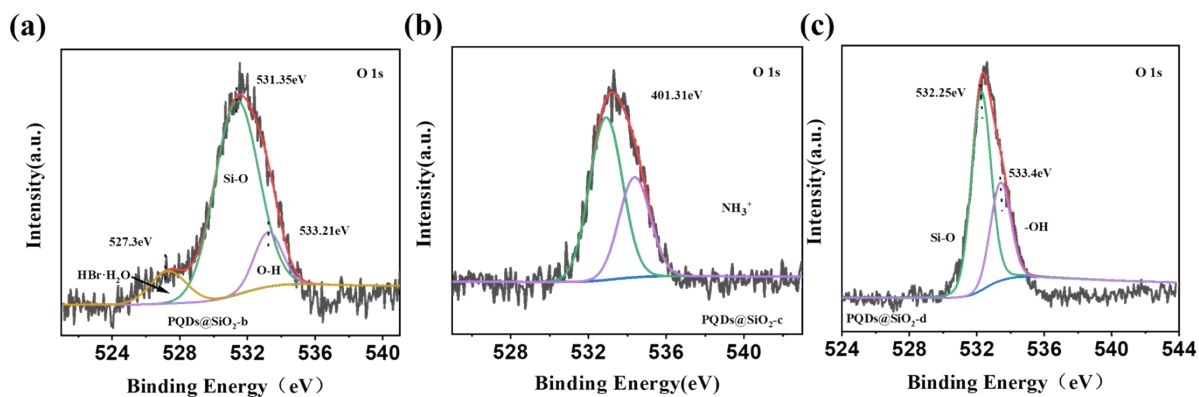
**Fig. S7.** High-resolution Cs 3d spectra of (a) PQDs@SiO<sub>2</sub>-b, (b) PQDs@SiO<sub>2</sub>-c, and (c) PQDs@SiO<sub>2</sub>-d.



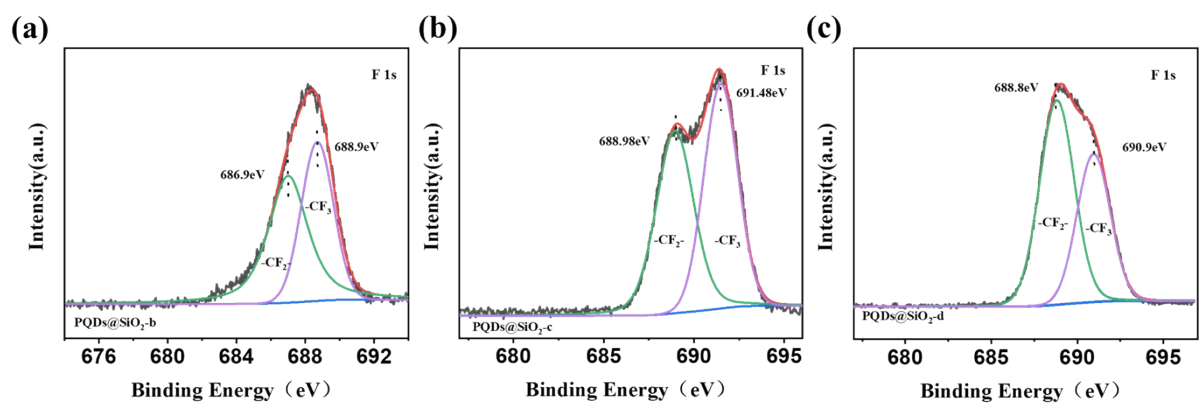
**Fig. S8.** High-resolution Pb 4f spectra of (a) PQDs@SiO<sub>2</sub>-b, (b) PQDs@SiO<sub>2</sub>-c, and (c) PQDs@SiO<sub>2</sub>-d.



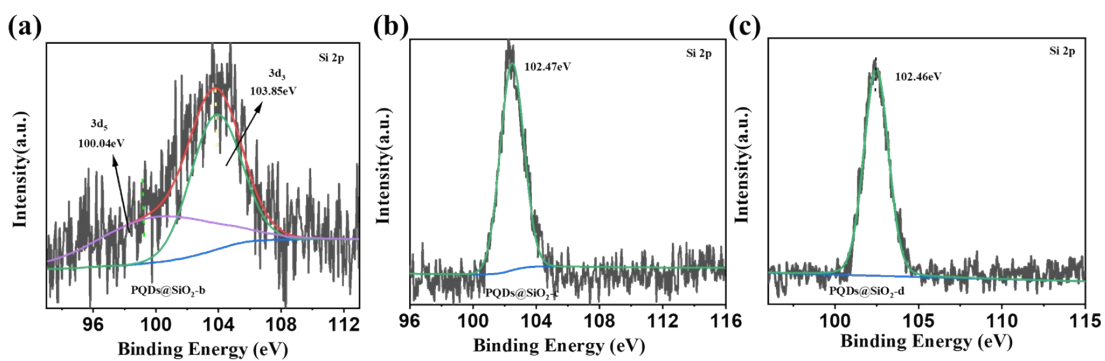
**Fig. S9.** High-resolution N 1s spectra of (a) PQDs@SiO<sub>2</sub>-b, (b) PQDs@SiO<sub>2</sub>-c, and (c) PQDs@SiO<sub>2</sub>-d.



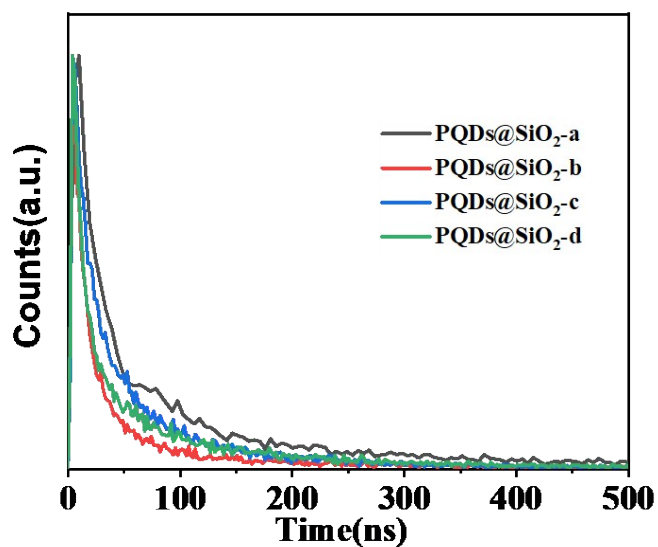
**Fig. S10.** High-resolution O 1s spectra of d) PQDs@SiO<sub>2</sub>-b, e) PQDs@SiO<sub>2</sub>-c, and f) PQDs@SiO<sub>2</sub>-d.



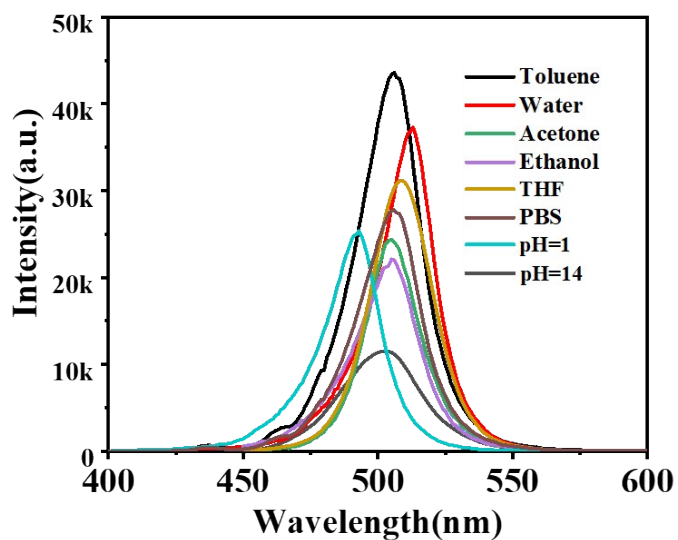
**Fig. S11.** High-resolution F 1s spectra of g) PQDs@SiO<sub>2</sub>-b, h) PQDs@SiO<sub>2</sub>-c, and i) PQDs@SiO<sub>2</sub>-d.



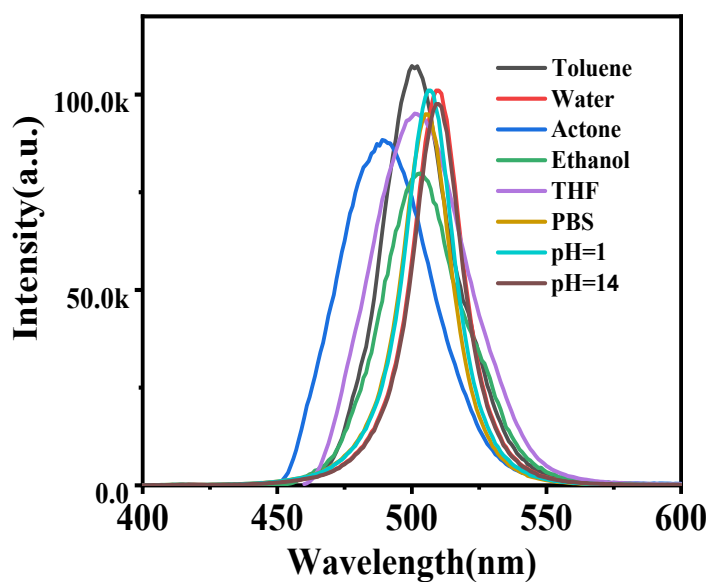
**Fig. S12.** High-resolution Si 2p spectra of j) PQDs@SiO<sub>2</sub>-b, k) PQDs@SiO<sub>2</sub>-c, and l) PQDs@SiO<sub>2</sub>-d.



**Fig. S13.** Time-resolved FL decay curves of PQDs@SiO<sub>2</sub>-a, PQDs@SiO<sub>2</sub>-b, PQDs@SiO<sub>2</sub>-c, and PQDs@SiO<sub>2</sub>-d.

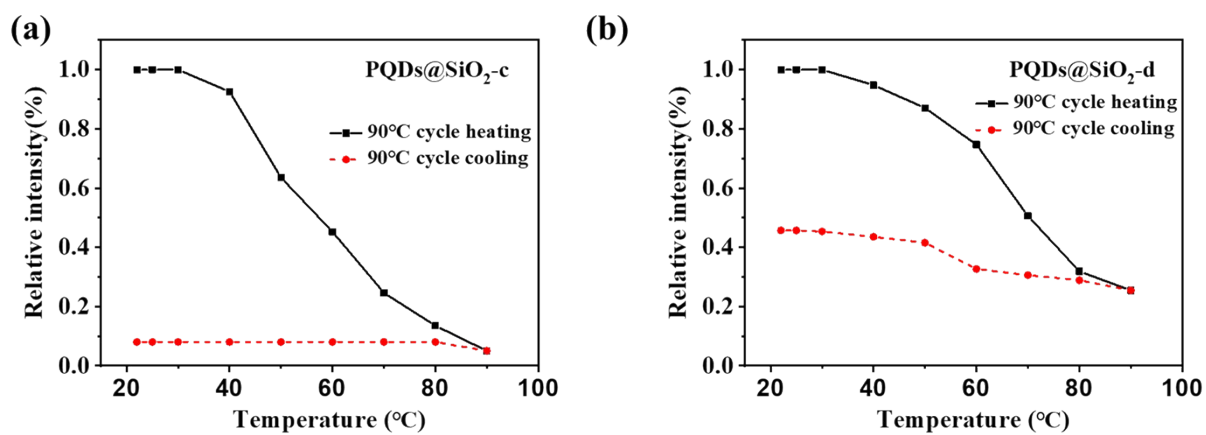


**Fig. S14.** PL spectra of PQDs@SiO<sub>2</sub>-c (1.0 mg mL<sup>-1</sup>) in toluene, water, THF, acetone, ethanol, PBS buffer solution, HCl solution (pH=1) and NaOH solution (pH=14).



**Fig. S15.** PL spectra of PQDs@SiO<sub>2</sub>-d (1.0 mg mL<sup>-1</sup>) in toluene, water, THF, acetone, ethanol, PBS buffer solution, HCl solution (pH=1) and NaOH solution (pH=14).





**Fig. S16.** Temperature-dependent PL intensity of (a) PQDs@SiO<sub>2</sub>-c and (b) PQDs@SiO<sub>2</sub>-d in water (1.0 mg mL<sup>-1</sup>).

**Table S1.** Experimental conditions of preparing samples *via* LARP method.<sup>a</sup>

| Samples                  | Ligand in precursors     |             |                     |                   |                    | Ligand in nucleation solvent |                |
|--------------------------|--------------------------|-------------|---------------------|-------------------|--------------------|------------------------------|----------------|
|                          | PbBr <sub>2</sub><br>(g) | CsBr<br>(g) | APTES<br>( $\mu$ L) | HBr<br>( $\mu$ L) | PFMS<br>( $\mu$ L) | NH <sub>2</sub> -PEG<br>(mg) | Si-PEG<br>(mg) |
| PQDs@SiO <sub>2</sub> -a | 0.146                    | 0.042       | 100                 | 20                | none               | none                         | none           |
| PQDs@SiO <sub>2</sub> -b | 0.146                    | 0.042       | 100                 | 20                | 250                | none                         | none           |
| PQDs@SiO <sub>2</sub> -c | 0.146                    | 0.042       | 100                 | 20                | 250                | 5                            | none           |
| PQDs@SiO <sub>2</sub> -d | 0.146                    | 0.042       | 100                 | 20                | 250                | none                         | 15             |

<sup>a</sup> Precursor solvent: DMF. Nucleation solvent: toluene. Temperature: room temperature.

**Table S2.** Cs/Pb, Pb/Br, and Cs/Pb/Br ratios of PQDs@SiO<sub>2</sub>-b, PQDs@SiO<sub>2</sub>-c, and PQDs@SiO<sub>2</sub>-d measured by XPS.

| Samples                  | Cs/Pb  | Pb/Br  | Cs/Pb/Br     |
|--------------------------|--------|--------|--------------|
| PQDs@SiO <sub>2</sub> -b | 1:1.3  | 1:4.34 | 1:1.3:5.64   |
| PQDs@SiO <sub>2</sub> -c | 1:2.56 | 1:4.49 | 1:2.56:11.51 |
| PQDs@SiO <sub>2</sub> -d | 1:0.79 | 1:4.72 | 1:0.79:3.73  |

**Table S3.** Summary of time-resolved FL decay measurements, where the lifetimes of samples are tested in toluene solution.  $\tau_1$  and  $\tau_2$  are the detailed recombination lifetimes, A and B represent the ratio of component contribution to the decay.  $k_f$  and  $\Sigma ki$  represent the radiative recombination and the non-radiative recombination rate constant.

| Samples                  | $\tau_1$ (ns) | A%    | $\tau_2$ (ns) | B%    | $k_f$                 | $\Sigma ki$           |
|--------------------------|---------------|-------|---------------|-------|-----------------------|-----------------------|
| PQDs@SiO <sub>2</sub> -a | 45.92         | 43.61 | 276.64        | 56.39 | $2.56 \times 10^{-3}$ | $1.44 \times 10^{-3}$ |
| PQDs@SiO <sub>2</sub> -b | 18.42         | 53.23 | 142.47        | 46.27 | $7.74 \times 10^{-3}$ | $0.16 \times 10^{-3}$ |
| PQDs@SiO <sub>2</sub> -c | 19.27         | 34.25 | 142.31        | 65.75 | $4.54 \times 10^{-3}$ | $3.15 \times 10^{-3}$ |
| PQDs@SiO <sub>2</sub> -d | 24.53         | 42.46 | 112.67        | 57.54 | $9.26 \times 10^{-3}$ | $0.70 \times 10^{-3}$ |

**Table S4.** Overview and comparison of the PL spectroscopic results from Fig. S14 of PQDs@SiO<sub>2</sub>-c in toluene, water, THF, acetone, ethanol, PBS buffer solution, HCl solution(pH=1) and NaOH solution(pH=14) (1.0 mg mL<sup>-1</sup>).

| Solution | Peak (nm) | Intensity | Ratio |
|----------|-----------|-----------|-------|
| Toluene  | 505       | 43399     | 1     |
| Water    | 512       | 37091     | 0.85  |
| THF      | 509       | 31178     | 0.72  |
| Acetone  | 505       | 24318     | 0.56  |
| Ethanol  | 505       | 22027     | 0.51  |
| PBS      | 506       | 27555     | 0.63  |
| pH=1     | 492       | 25182     | 0.58  |
| pH=14    | 506       | 11378     | 0.26  |

**Table S5.** Overview and comparison of the PL spectroscopic results from Fig. S15 of PQDs@SiO<sub>2</sub>-d in toluene, water, THF, acetone, ethanol, PBS buffer solution, HCl solution (pH=1) and NaOH solution (pH=14) (1.0 mg mL<sup>-1</sup>).

| Solution | Peak (nm) | Intensity | Ratio |
|----------|-----------|-----------|-------|
| Toluene  | 505       | 107240    | 1     |
| Water    | 510       | 101000    | 0.94  |
| THF      | 501       | 95108     | 0.89  |
| Acetone  | 489       | 88370     | 0.82  |
| Ethanol  | 506       | 79810     | 0.74  |
| PBS      | 512       | 95067     | 0.87  |
| pH=1     | 506       | 101536    | 0.95  |
| pH=14    | 510       | 97663     | 0.91  |

## REFERENCES

- [1] Y. Chen, X. Song, F. Peng, J. Li, Preparation of Monomethoxy Poly(ethylene glycol) Amine, *Fine Chemicals* **2015**, 32, 434.