Suppressed blinking behavior of CdSe/CdS QDs by polymer coating

Supplementary Material

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Experimental section

Materials and reagents.

Cadmium oxide (CdO, 99.99%), selenium (Se, 99.999%), trioctylphosphine (TOP, 90%), oleylamine (OAm, 70%), stearic acid (95%), hexadecylamine (90%), oleic acid (90%), 1–octadecene (ODE, 90%), sulfur (99.9%), *p*–phenylenediamine (*p*–PDA, ≥99.0%), hexachlorocyclotriphosphazene (HCCP, 99.95%), dithiothreitol (DTT, ≥99.5%), hexamethylenediamine (HDA, 98%), and poly (methyl methacrylate) (PMMA, average M_w ～ 15000 by GPC), were purchased from Sigma–Aldrich. All the preparations of the stock solutions were performed in a nitrogen–filled glovebox.

Preparation of the precursors stock solutions for the SILAR growth.

The preparation of 0.1 mol/L cadmium–oleate precursor solution: 2.5 mmol of CdO, 7 mL of oleic acid and 18 mL of ODE were loaded into a 100 mL three–neck flask. The mixture was degassed at 80 ^{o}C under vacuum for 30 min. Under argon flux, the temperature was heated to about 200 ^{o}C and kept at this temperature for 1 h in order to obtain a yellow clear solution. Then, the stock solution was allowed to cool to about 80 ^{o}C and degassed under vacuum for 30 min.

The preparation of 0.1 mol/L sulfur precursor solution: 5.0 mmol of element sulfur and 50 mL ODE were loaded into a 100 mL three–neck flask. The mixture was degassed at 80 ^{o}C under vacuum for 30 min. Under argon flux, the temperature was heated to about 180 ^{o}C and kept at this temperature for 0.5 h in order to obtain a yellow clear solution. Then, the stock solution was allowed to cool to about 80 ^{o}C and degassed under vacuum for 30 min.

Calculation of the amount of the precursors solutions for the SILAR growth.

The calculation was based the volume of CdS molecule.[1, 2]

The estimate size of CdSe core QDs:

D_0=3.11 nm, $R_0=\frac{3.11}{2}$=1.5550 nm,

The estimated amount of CdSe QDs:

$n_1=1.0358\times10^{-7}$ mol,

Lattice constant of CdS:

For wurtzite: a=0.4160 nm, c=0.6756 nm,

For zinc blende: a=0.5832 nm,

The volume of CdS molecule:

For wurtzite: $V_{\mathrm{CdS}}=\frac{1}{2}\times(\frac{\sqrt{3}}{2}a)\times a\times c=\frac{1}{2}\times(\frac{\sqrt{3}}{2}0.4160)\times0.4160\times0.6756=0.0506\,\mathrm{nm}^3$,

For zinc blende: $V_{\mathrm{CdS}}=\frac{a^3}{4}=\frac{(0.5832)^3}{4}=0.0496\,\mathrm{nm}^3$,

Therefore, we take $V_{\mathrm{CdS}}=0.050\,\mathrm{nm}^3$;

The average thickness (d) of one monolayer CdS:

For wurtzite: $d=c\frac{1}{2}=0.6756\times\frac{1}{2}=0.3378\,\mathrm{nm}$,

For zinc blende: $d=a\frac{\sqrt{3}}{3}=0.5832\times\frac{\sqrt{3}}{3}=0.3367\,\mathrm{nm}$,

Therefore, we take d=0.337 nm;

The amount of Cd and S precursor for the first layer CdS (1 ML):

The volume of the first CdS monolayer:

$V_1=\frac{4\pi}{3}\times(R_1^3\text{-}R_0^3)$, here: R_0=1.555 nm, R_1=1.892 nm,

$V_1=\frac{4}{3}\times3.14\times(1.8920^3\text{-}1.5550^3)=12.613\ \mathrm{nm}^3$;

The amount of CdS molecules in one core/shell particle:

$n_2=\frac{V_1}{V_{\mathrm{CdS}}}=\frac{12.613\,\mathrm{nm}^3}{0.05\,\mathrm{nm}^3}=252.26$ (CdS molecule);

The amount of Cd or S precursor for the first layer CdS growth:

$A_1=n_1\times n_2=1.0358\times10^{-7}\,\mathrm{mol}\times252.26=2.61\times10^{-5}\,\mathrm{mol}=0.026\,\mathrm{mmol}$;

The injected amount of the precursors for the others monolayer followed a square progression.

2 monolayer CdS: $A_2 = A_1 \times \frac{V_2}{V_1} = 0.026 \times (2.229^3\text{-}1.892^3)/(1.892^3\text{-}1.555^3) = 0.037 \text{ mmol}$;

3 monolayer CdS: $A_3 = A_1 \times \frac{V_3}{V_1} = 0.026 \times (2.566^3\text{-}2.229^3)/(1.892^3\text{-}1.555^3) = 0.050 \text{ mmol}$;

4 monolayer CdS: $A_4 = A_1 \times \frac{V_4}{V_1} = 0.026 \times (2.903^3\text{-}2.566^3)/(1.892^3\text{-}1.555^3) = 0.065 \text{ mmol}$;

5 monolayer CdS: $A_5 = A_1 \times \frac{V_5}{V_1} = 0.026 \times (3.240^3\text{-}2.903^3)/(1.892^3\text{-}1.555^3) = 0.082 \text{ mmol}$;

Synthesis of CdSe QDs.

Typically, 0.40 mmol CdO and 1.75 mmol stearic acid were mixed with 3 mL ODE in a 50 mL three–neck flask. The mixture was degassed at 100 °C under vacuum for 30 min. Under argon flux, the temperature was heated to about 270 °C to obtain a colorless clear solution. At this temperature, a solution containing 0.40 mmol of Se dissolved in 3.5 mL TOP, 1 mL OAm and 1 mL ODE was quickly injected into the flask. After the injection, the temperature was adjusted to 260 °C and kept for 1 min. After this time, the heating mantle was removed and the reaction mixture was allowed to cool to room temperature, and an extraction procedure was used to purify the QDs from side products and unreacted precursors.[3, 4] The particle concentration of the purified CdSe QDs in hexane was measured using Lambert–Beer's law with the reported extinction coefficients of CdSe QDs.[5] Typically this reaction generates CdSe QDs of about 3.2 nm in size with the first absorption peak around 550 nm.

Synthesis of CdSe/CdS QDs.

Briefly, CdSe QDs (*ca.* 3.2 nm in diameter, 100 nmol of particles) dissolved in 1 mL hexane were mixed with 2 mL of OAm and 4 mL of ODE in a 50 mL three–neck flask. The system was kept at 100 °C under vacuum for 30 min to remove the hexane and other undesired materials of low vapor pressure. Then the flask was heated to 240 °C under argon flow where the shell growth was performed. CdS shell was grown monolayer by monolayer, by alternating injections of Cd–oleate and sulfur precursors with the use of a syringe pump. The precursor's amounts were calculated from the core size and desired shell thickness. The growth time was 15 min after each injection.

When the desired CdS shell thickness was achieved, the growth solution was cooled to room temperature. The resulting CdSe/CdS QDs were precipitated by adding acetone, and then re–dispersed in hexane. The QDs were further purified by precipitation–redispersion for two more rounds and finally suspended in 6 mL of toluene.

Synthesis of CdSe/CdS/polymer QDs.

The core/shell/shell structured CdSe/CdS/polymer QDs were prepared by the solvothermal method. Briefly, 2 mL of CdSe/CdS QDs (dispersed in toluene) and 30 mL of tetrahydrofuran were added to a polytetrafluoroethylene–lined autoclave containing 0.2 mL of HCCP (0.01 mol/L), 0.6 mL of DTT (0.01 mol/L) and 100 μL of triethylamine (TEA). The reaction solution was purged with argon for 30 minutes to completely remove oxygen. The polycondensation reaction was conducted at 150 ^{o}C in oil bath for 3 h. For the other polyphosphazene polymers, the DTT was replace by PDA or HDA. Herein, for easy writing, we defined the final polyphosphazene polymers as follows, poly–(cyclotriphosphazene–*co*–dithiothreitol) (abbreviated as PDTT hereafter), poly–(cyclotriphosphazene–*co*–phenylenediamine) (abbreviated as PPDA hereafter), poly–(cyclotriphosphazene–*co*–hexamethylenediamine) (abbreviated as PHDA hereafter).

Characterization of QDs.

UV–vis absorption spectra were obtained using a UV/Vis–3501 spectrophotometer. PL spectra were obtained immediately after UV–vis measurements on an F–380 spectrometer (Tianjin Gangdong SCI & Tech. Development Co., Ltd., China). Fourier transform infrared (FTIR) spectra were recorded on a Spectrum 100 instrument (Perkin Elmer, Inc., U.S.A.), the QDs solution was uniformly coated on the KBr pellet, baked under infrared lamp to eliminate excess solvent before analyzing. Transmission electron microscopy (TEM) observations were performed on a JEM–2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. Thermogravimetric analyses (TGA) were investigated on a Q5000IR thermogravimetric analyzer (TA Instruments, U.S.A.) with a heating rate of 20 ^{o}C/min in a nitrogen flow. Lifetime measurement was carried out using an FLS920 Fluorescence Lifetime and Steady State Spectrometer (Edinburgh Instruments, UK). The fluorescence QYs of QDs were measured according to the method described in the reference. Rhodamine 6G (dissolved in ethanol) was chosen as a reference standard (QY = 95%).[3]

The single–particle fluorescence trajectories were acquired with a total internal reflection fluorescence microscopy (TIRFM) imaging system based on an Olympus IX–71 inverted microscope (Olympus Optical Co., Japan) with an oil immersion objective (NA 1.45/60x, Olympus Optical Co., Japan).[6] In this study, QDs samples were excited with a 488 nm continuous-wave argon ion laser (ILT Ion Laser Technology, Shanghai, China), and the laser power monitored in front of the microscopy objective (NA 1.45/60×, Olympus Optical Co., Japan) was measured to be 0.22 mW after it is attenuated. Fluorescence from the sample was collected by the same objective, separated from the excitation light by a dichroic mirror (ZT488rdc, Chroma Technology Corp, U.S.A.) and an emission filter (595AF60, Omega Optical, U.S.A.), and then focused into an electron–multiplying charge coupled device

(EMCCD) with a frame device (Evolve 512, Photometrics, U.S.A.). The frame transfer device has an imaging array of 512 × 512 pixel with 16 × 16 μm/pixel. The exposure time was set at 30 ms for each frame. The image acquisition and data processing were performed using the ImageJ software (National Institutes of Health, free software, http://rsb.info.nih.gov/ij/), and MATLAB (The MathWorks Inc., U.S.A.). All the single–particle PL emission measurements were performed at room temperature. The coverslips (24 × 50 × 0.1 mm^3, Fisher, U.S.A.) were thoroughly cleaned by piranha solution and washed with ultrapure water (Millpore, U.S.A.) and then dried in a jet of argon flow. The sample for single–particle imaging was prepared by spin casting a diluted solution of the newly–prepared QDs in chloroform containing 2% PMMA (g/mL) on a glass coverslip, and left for complete drying.

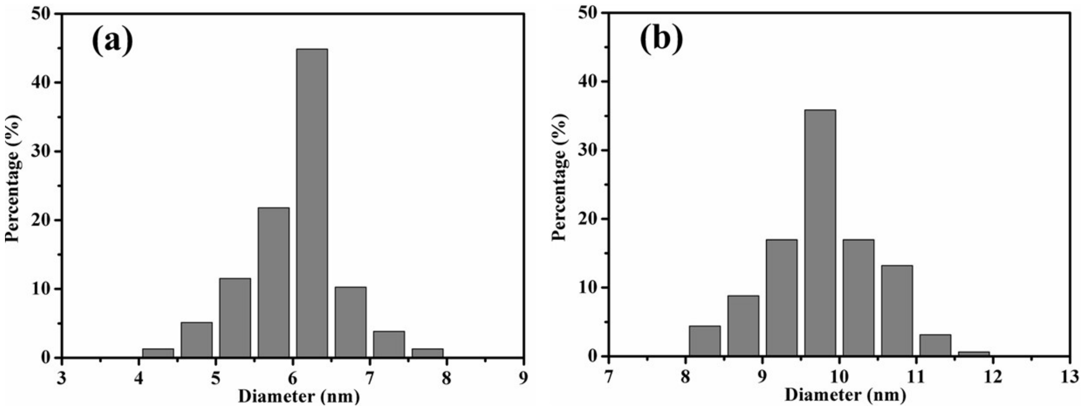

Fig. S1 Particle distribution histograms of CdSe/CdS QDs. To build the histograms, the longest dimension for over 200 particles in each sample were measured. **(a)** Histogram of CdSe/CdS QDs with an average diameter of 6.0 nm (CdSe core diameter of 3.2 nm, CdS shell thickness of 1.4 nm); **(b)** Histogram of CdSe/CdS QDs with an average diameter of 9.8 nm (CdSe core diameter of 3.2 nm, CdS shell thickness of 3.3 nm).

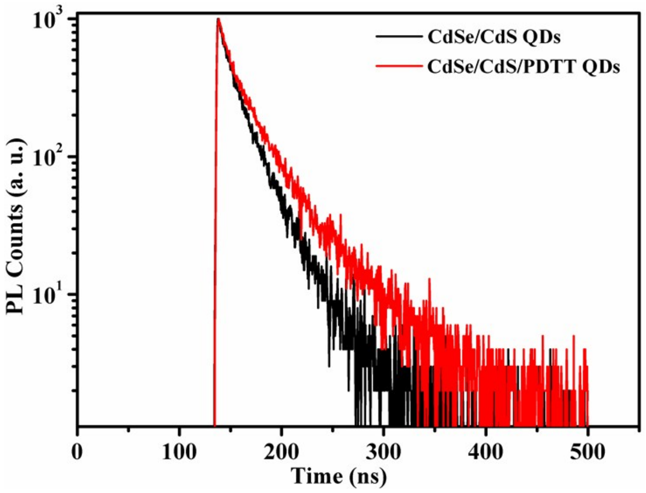

Fig. S2 Representative transient PL decays for CdSe/CdS QDs and CdSe/CdS/PDTT QDs.

FTIR analysis for the polyphosphazene polymers of PPDA and PHDA.

As shown in Fig. S3(b), the two sharp stretching vibration peaks at 1630 cm^{-1} and 1528 cm^{-1} were the characteristic absorption of phenyl group of PDA. The peak at 3349 cm^{-1} represented the N–H stretching vibration absorption of the primary amino group ($–NH_2$). For CdSe/CdS/PPDA QDs [Fig. S3(d)], the absorption peaks at *ca.* 3000–3300 cm^{-1} were increased, which indicated the introduction of $–NH_2$ or –OH group. The strong absorption peak at 1125 cm^{-1} corresponded to the skeleton structure of cyclotriphosphazene, the peaks at 1660 cm^{-1} and 1460 cm^{-1} were associated with the phenyl group, these result confirmed the product contained both the structure units of HCCP and PDA.

In the FTIR spectra of HDA [Fig. S4(b)], the strong and sharp absorption peak at 3337 cm^{-1} were assigned to the stretching vibration peaks N–H ($–NH_2$). For CdSe/CdS/PHDA QDs [Fig. S4(d)], the strong absorption peak between 3300 cm^{-1} and 3600 cm^{-1} and the characteristic absorption of cyclotriphosphazene at 1112 cm^{-1}, proving the occurrence of polycondensation between HCCP and HDA. Furthermore, by comparison of the spectra of HCCP and CdSe/CdS/PDTT QDs, it is found that the strong absorption of the P–Cl band of HCCP at 607 cm^{-1} greatly decreased after the polycondensation.

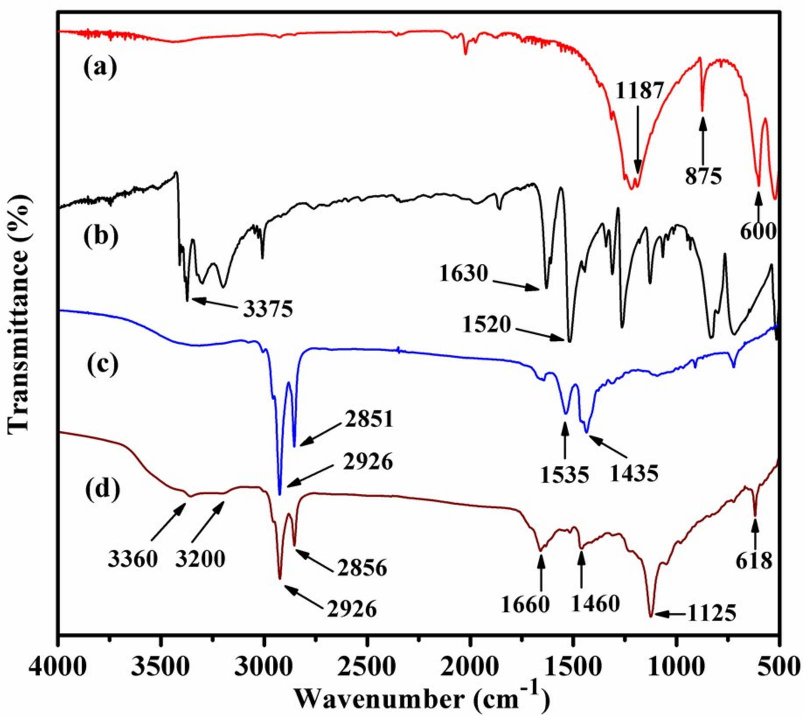

Fig. S3 FTIR spectra of HCCP (a), *p*–phenylenediamine (b), CdSe/CdS QDs (c), CdSe/CdS/PPDA QDs (d). (Solvent: tetrahydrofuran, wavelength range: 4000–500 cm^{-1}).

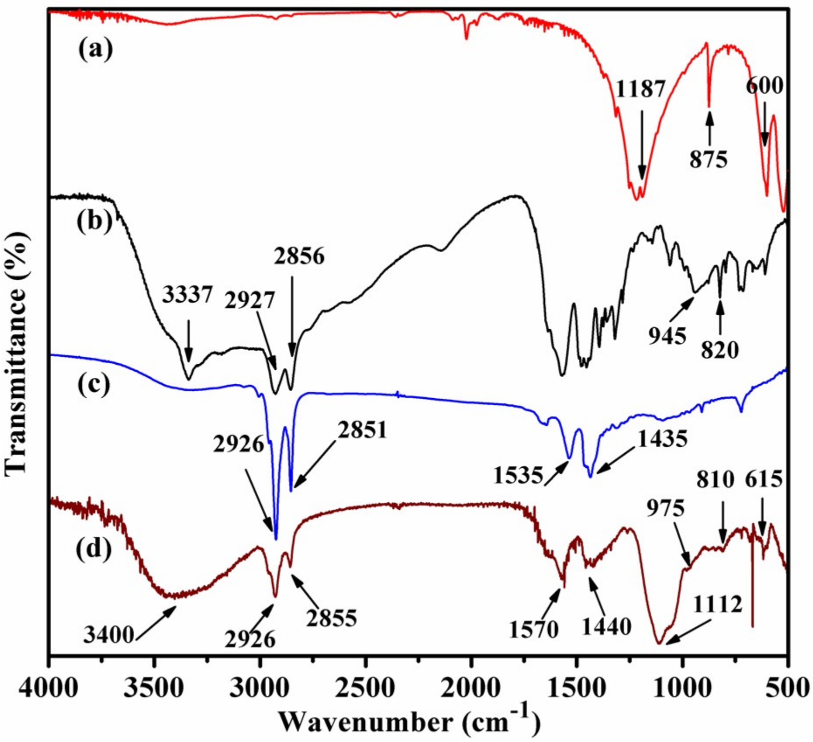

Fig. S4 FTIR spectra of HCCP (a), hexanediamine (b), CdSe/CdS QDs (c), CdSe/CdS/PHDA QDs (d). (Solvent: tetrahydrofuran, wavelength range: 4000–500 cm^{-1}).

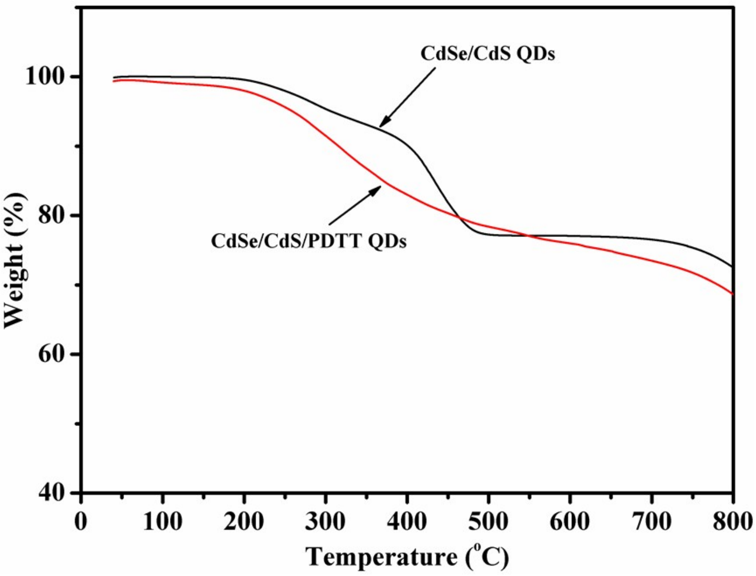

Fig. S5 TGA curves of CdSe/CdS QDs and CdSe/CdS/PDTT QDs.

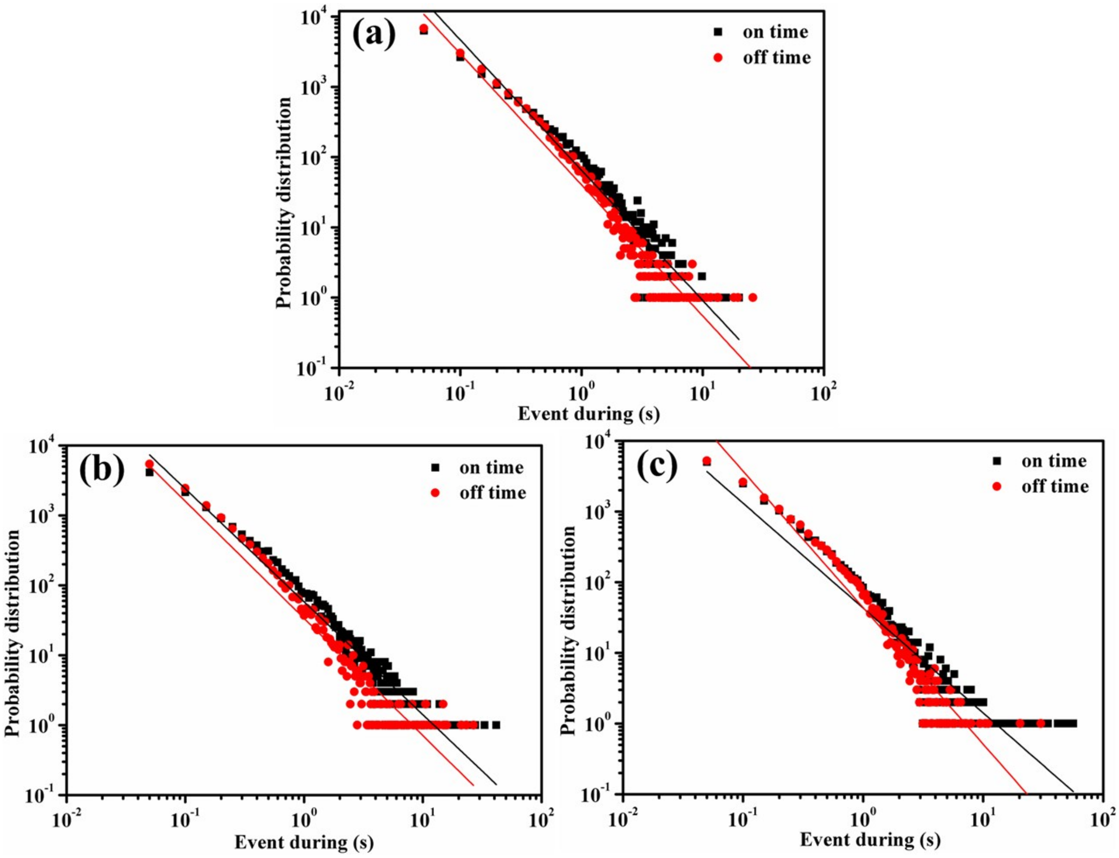

Fig. S6 Log–log scale of the probability densities of "on time" and "off time" for CdSe QDs (a) and CdSe/CdS QDs ((b) for 6.0 nm and (c) for 9.8 nm).

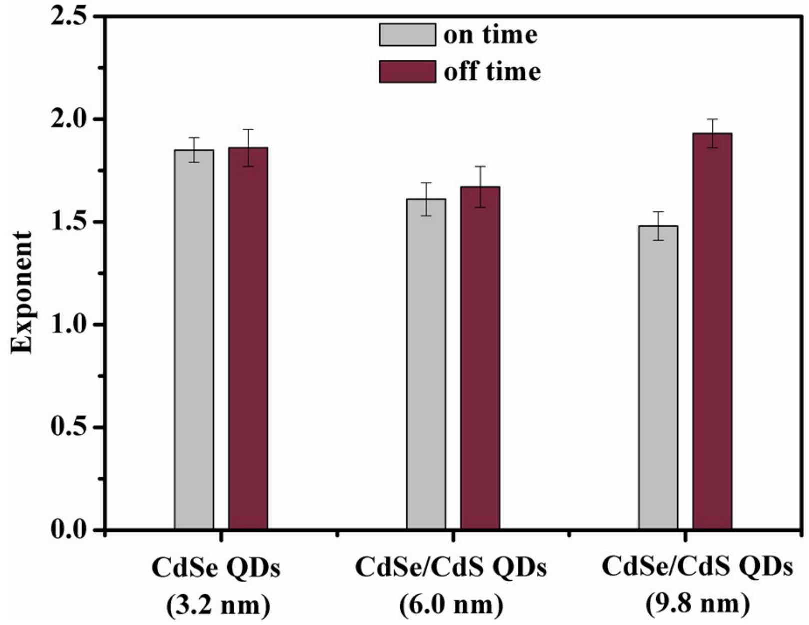

Fig. S7 Fitting results of the power law exponents ($m_{\mathrm{on/off}}$) of CdSe QDs and CdSe/CdS QDs extracted from Fig. S6.

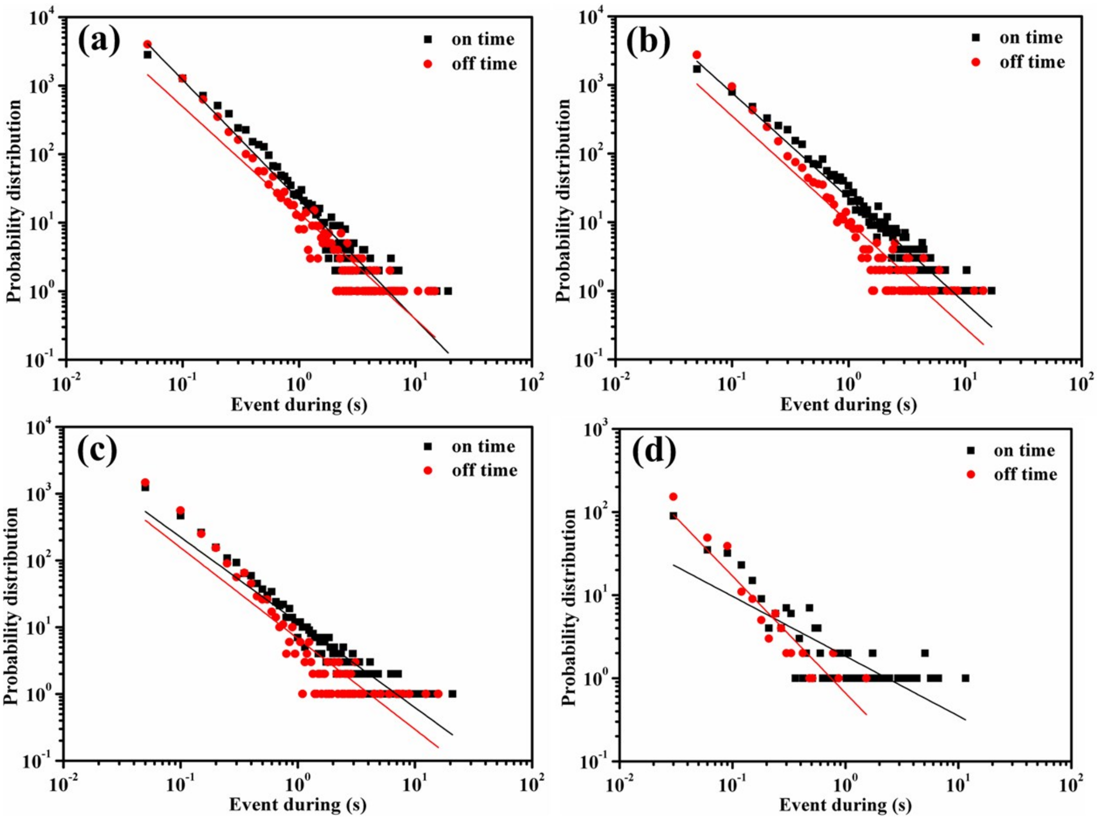

Fig. S8 Log–log scale of the probability densities of "on time" and "off time" for CdSe/CdS/PDTT QDs. (a)–(d) stands for QDs prepared with different molar ratios of HCCP:DTT (1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively).

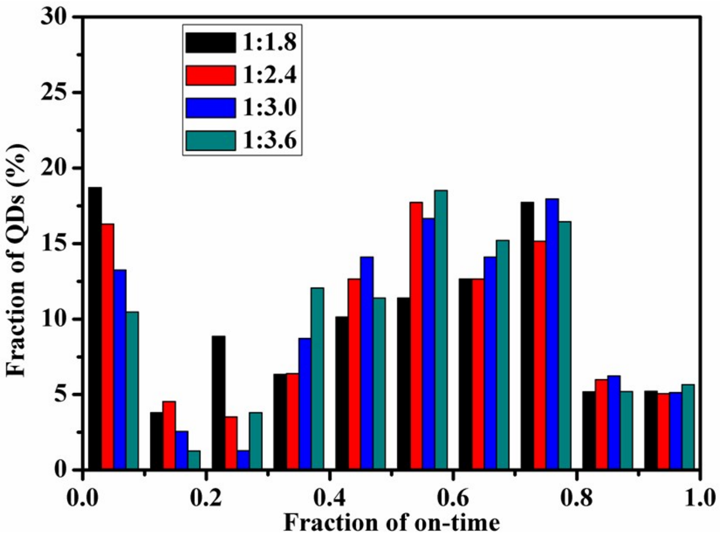

Fig. S9 "On time" distribution histogram for CdSe/PDTT QDs (0.2 mL for HCCP, and 0.36, 0.48, 0.60, 0.72 mL for DTT). The molar ratios of HCCP:DTT were 1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively.

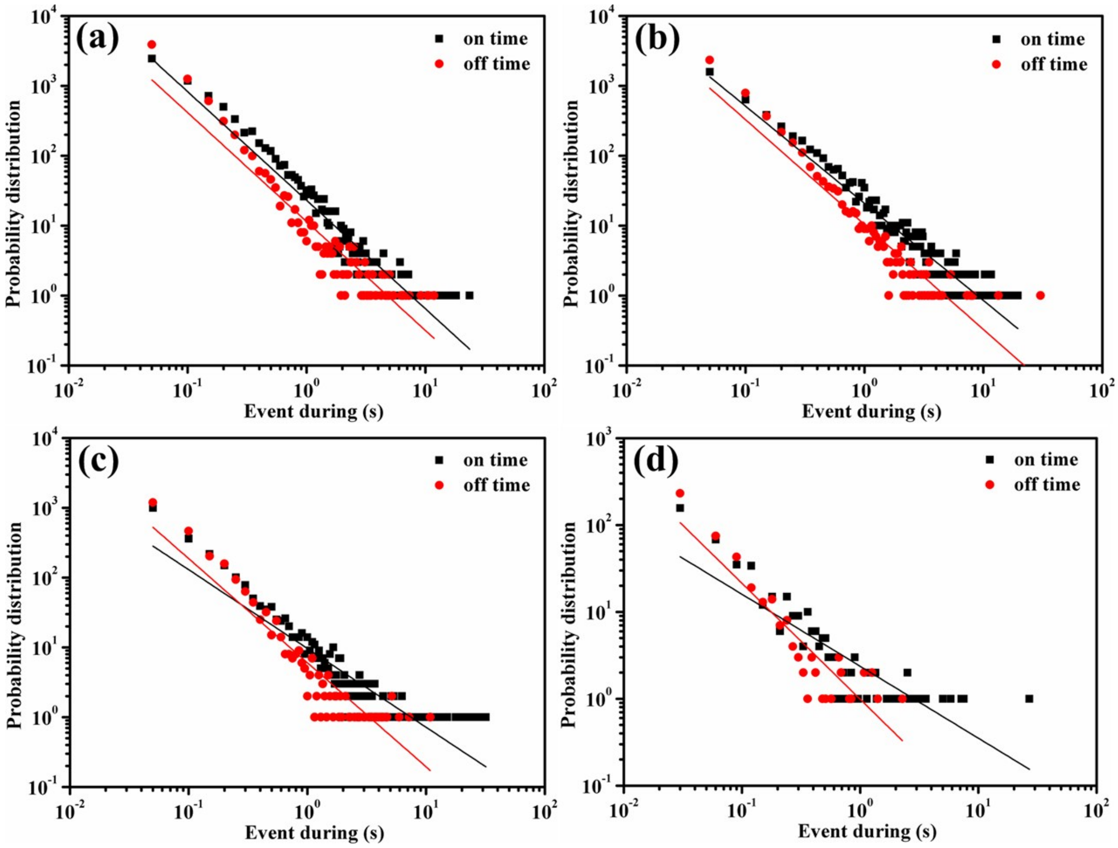

Fig. S10 Log–log scale of the probability densities of "on time" and "off time" for CdSe/CdS/PPDA QDs. (a)–(d) stands for QDs prepared with different molar ratios of HCCP:PDA (1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively).

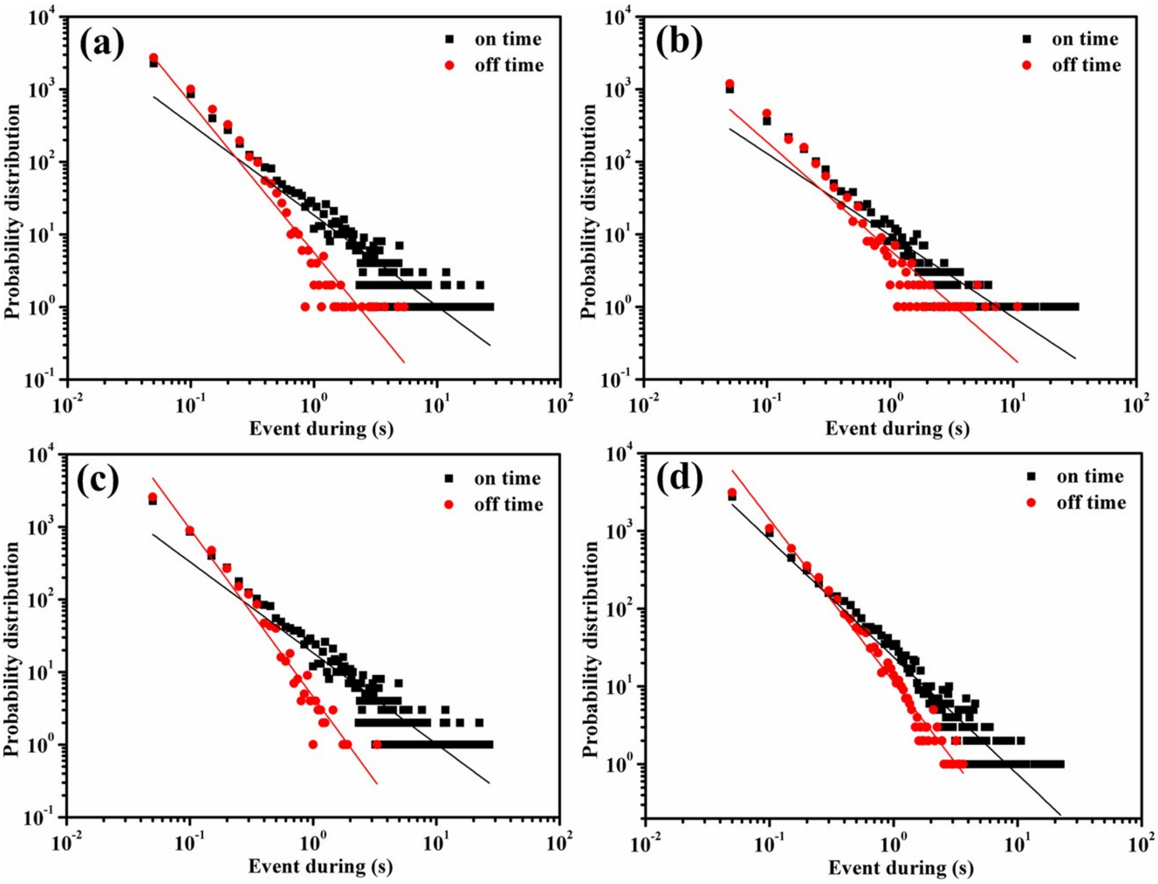

Fig. S11 Log–log scale of the probability densities of "on time" and "off time" for CdSe/CdS/PHDA QDs. (a)–(d) stands for QDs prepared with different molar ratios of HCCP:HDA (1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively).

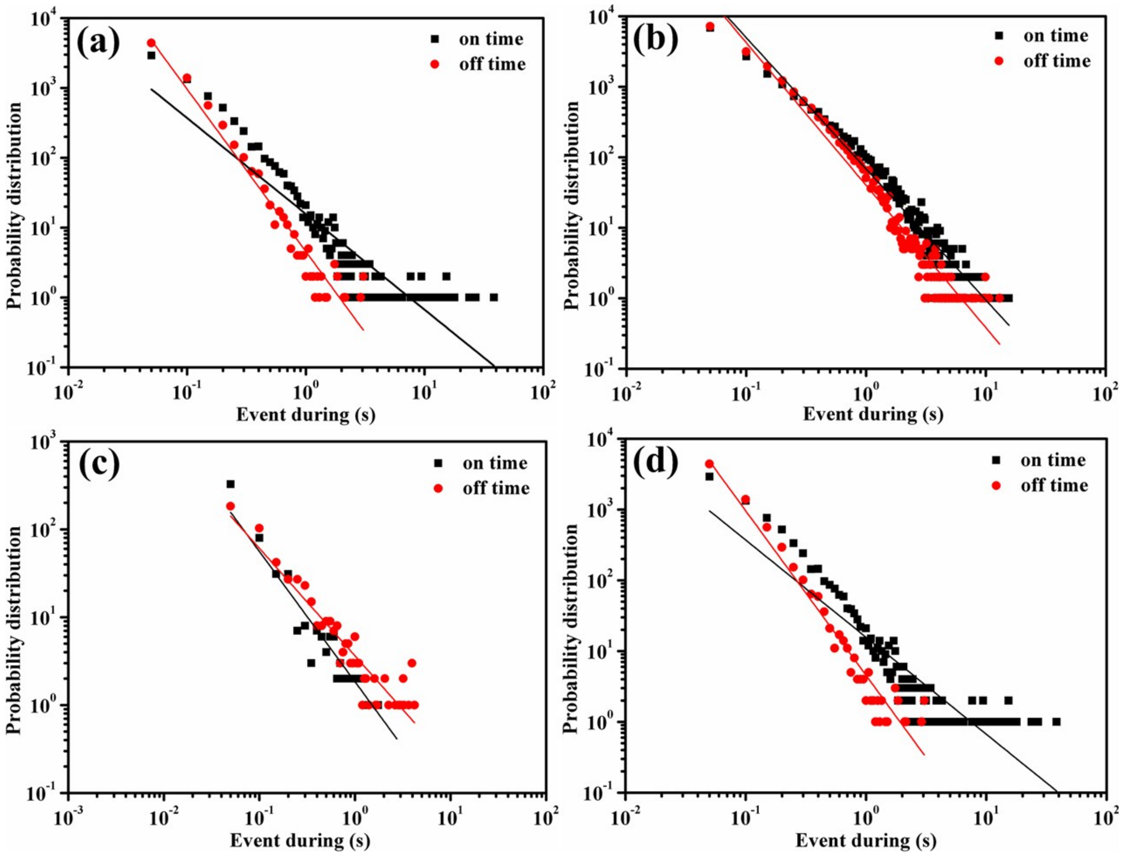

Fig. S12 Log–log scale of the probability densities of "on time" and "off time" for CdSe/CdS/PDTT QDs. (a)–(d) stands for QDs prepared with different molar ratios of HCCP:DTT (0.2:1, 0.4:1, 0.6:1, and 0.8:1, respectively).

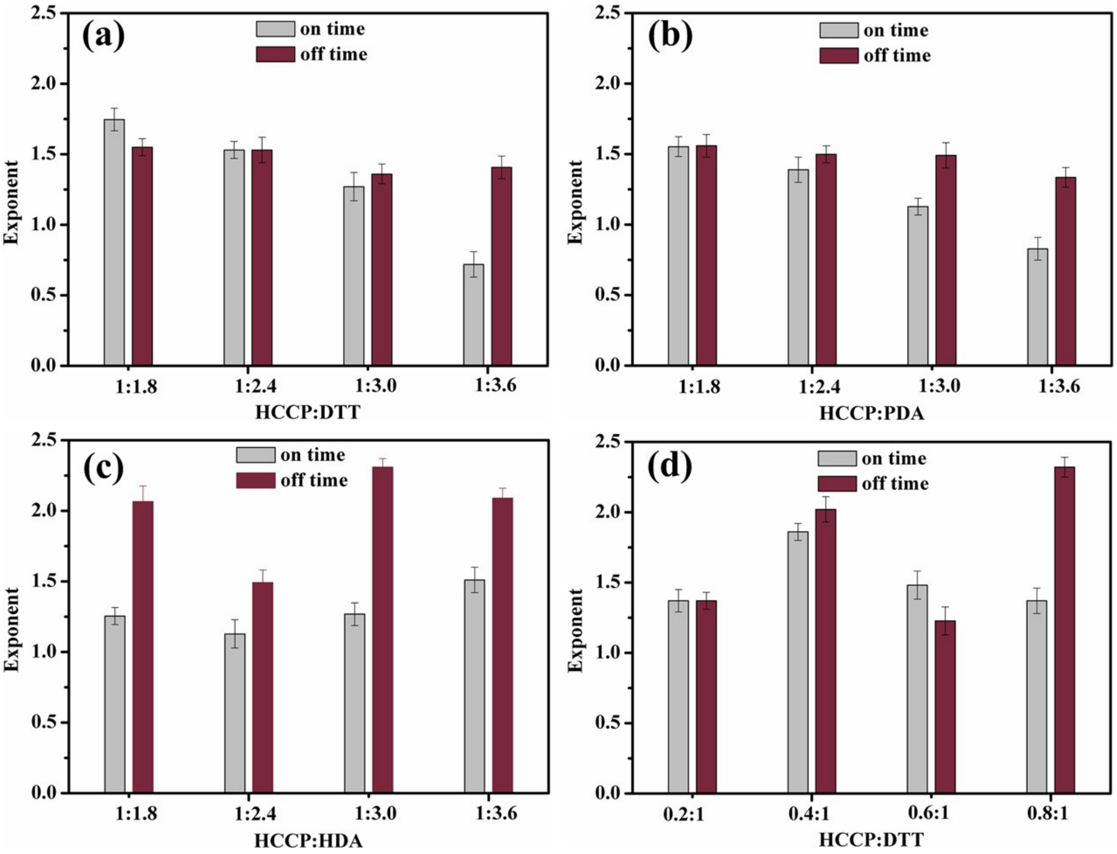

Fig. S13 Fitting results of the power law exponents ($m_{\mathrm{on/off}}$) of CdSe/CdS/polymer QDs extracted from Fig. S8, Fig. S10, Fig. S11, and Fig. S12.

References

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