Electronic Supplementary Information for

Effect of trifluoroacetic acid on InP/ZnSe/ZnS quantum dots: mimicking the surface trap and their effects on the photophysical properties

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1. Experimental Details

Experimental details

Synthesis of InP cores. Indium acetate and palmitic acid were dissolved in 1-octadecene in a 200 mL reaction flask and subjected to a vacuum state at 120 °C for 1 h. The molar ratio of indium to palmitic acid was 1:3. The atmosphere in the flask was exchanged with N_2. After the reaction flask was heated to 280 °C, a mixed solution of tris(trimethylsilyl)phosphine (TMS_3P) and trioctylphosphine (TOP) was rapidly injected, and the reaction proceeded for 20 min. The reaction mixture was subsequently rapidly cooled to 20 °C and acetone was added to produce nanocrystals, which were then separated by centrifugation and dispersed in toluene to obtain a toluene dispersion of InP core nanocrystals. The amount of the TMS3P was approximately 0.75 moles per one mole of indium.

ZnSe/ZnS shell coating. In a 200 mL reaction flask, zinc acetate and oleic acid were dissolved in trioctylamine (TOA) and the solution was subjected to vacuum at 120 °C for 10 min. The atmosphere in the reaction flask was replaced with N_2. While the resulting solution was heated to approximately 320 °C, a toluene dispersion of the InP cores was injected, and four different amounts of Se/TOP stock solution were injected into the reaction flask to vary the ZnSe shell thickness. A reaction was performed to obtain a reaction solution including a particle having a ZnSe shell disposed on the core. The total reaction time was 100 min. Subsequently, at the same temperature, the S/TOP stock solution was injected into the reaction mixture. A reaction was performed to obtain a resulting solution including a particle having a

ZnS shell disposed on the ZnSe shell. The total reaction time was 40 min and a total amount of the S used was approximately 12 moles per one mole of indium. An excess amount of ethanol was added to the final reaction mixture including the resulting InP/ZnSe/ZnS semiconductor nanocrystals, which was then centrifuged. After centrifugation, the supernatant was discarded and the precipitate was dried and dispersed in chloroform to obtain a QD solution.

Characterization. The size and chemical compositions of a series of InP/ZnSe/ZnS QDs were characterized using ICP-AES (Inductively coupled plasma atomic emission spectroscopy), TEM (transmission electron microscopy), and XPS (X-ray photoelectron spectroscopy).

Steady-state absorption measurements. UV/Vis/NIR absorption spectra were recorded on a commercial absorption spectrometer (Varian, Cary5000). Quartz cell (Hellma) with optical path length of 10 mm was used for all steady-state measurements.

Photoluminescence measurements. Photoluminescence spectra and lifetime were obtained using a commercial fluorescence lifetime spectrometer (PicoQuant, Fluotime 300). A 379 nm diode laser (PicoQuant) was used for photoexcitation.

Femtosecond transient absorption spectroscopy. A femtosecond time-resolved transient absorption (fs-TA) spectrometer consisted of optical parametric amplifiers (TOPAS, Light conversion) pumped by a Ti:sapphire regenerative amplifier system (Libra, Coherent) operating at an 1 kHz repetition rate and an optical detection system (Helios, Ultrafast

Systems). The generated OPA pulses had a pulse width of ~70 fs and an average power of 100 mW at 400 nm that were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (thickness = 3 mm) by focusing a small portion of the fundamental 800 nm pulses, which was picked off by a quartz plate before entering into the OPA. The time delay between the pump and probe beams was carefully controlled by allowing the pump beam to travel along a variable optical delay. Intensities of the spectrally dispersed WLC probe pulses were monitored using a high-speed spectrometer (Ultrafast Systems). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were alternately saved with or without the pump pulse. The transient absorption signals were recorded depending on the pump power from 30 to 700 μW.

XPS measurements. The chemical/electronic structures were characterized using X-ray photoelectron spectroscopy measurement (Quantera manufactured by ULVAC-PHI).

TEM measurements. TEM samples were prepared by the following sequence: as-synthesized QD particles in hexane were dispersed on the carbon film supported TEM mesh grid and then dried in an oven at 90 °C for 2 h. STEM-HAADF analysis was conducted by double Cs-corrected TEM (Titan3 60-300, FEI) at 300 keV.

ICP-AES measurements. The ICP-AES was carried out using ICPS-8100 (manufactured by Shimadzu). All the QDs (3~5 mg) in this study were diluted in HNO3 (50 mL). In the case of

TFA-added QDs, we inserted TFA into QD solution (chloroform) and evaporated the solvent to get a powder of QDs.

3. Supporting figures (Figures S1–S14, Tables S1 and S2).

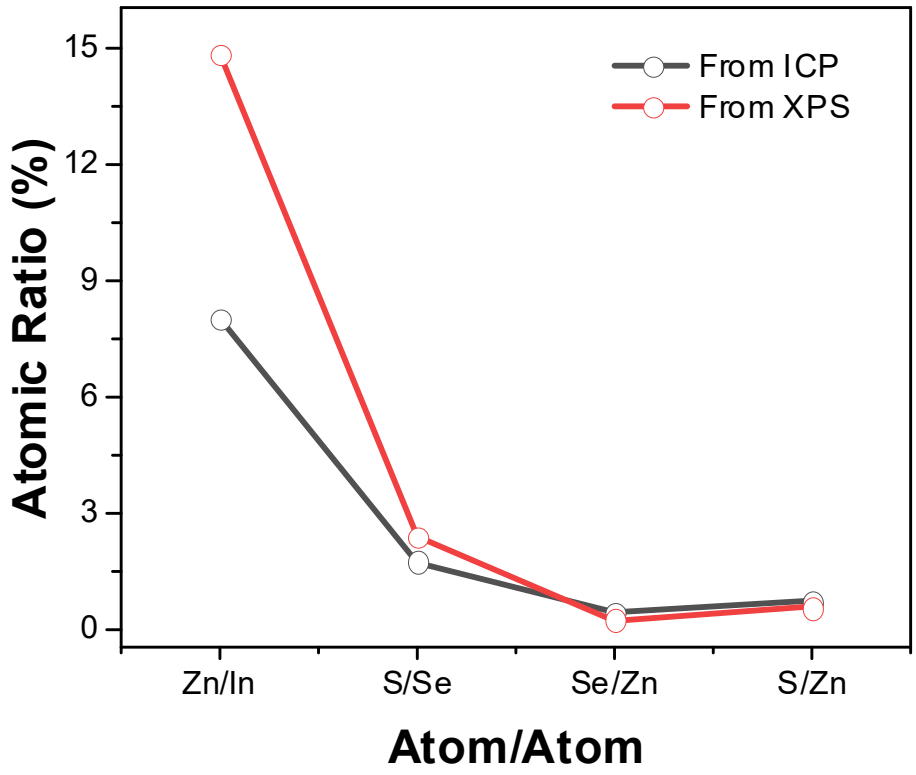

Figure S1. Atomic ratio of InP/ZnSe/ZnS QDs from inductively coupled plasma (ICP) (black) and X-ray photoelectron spectroscopy (XPS) (red) results.

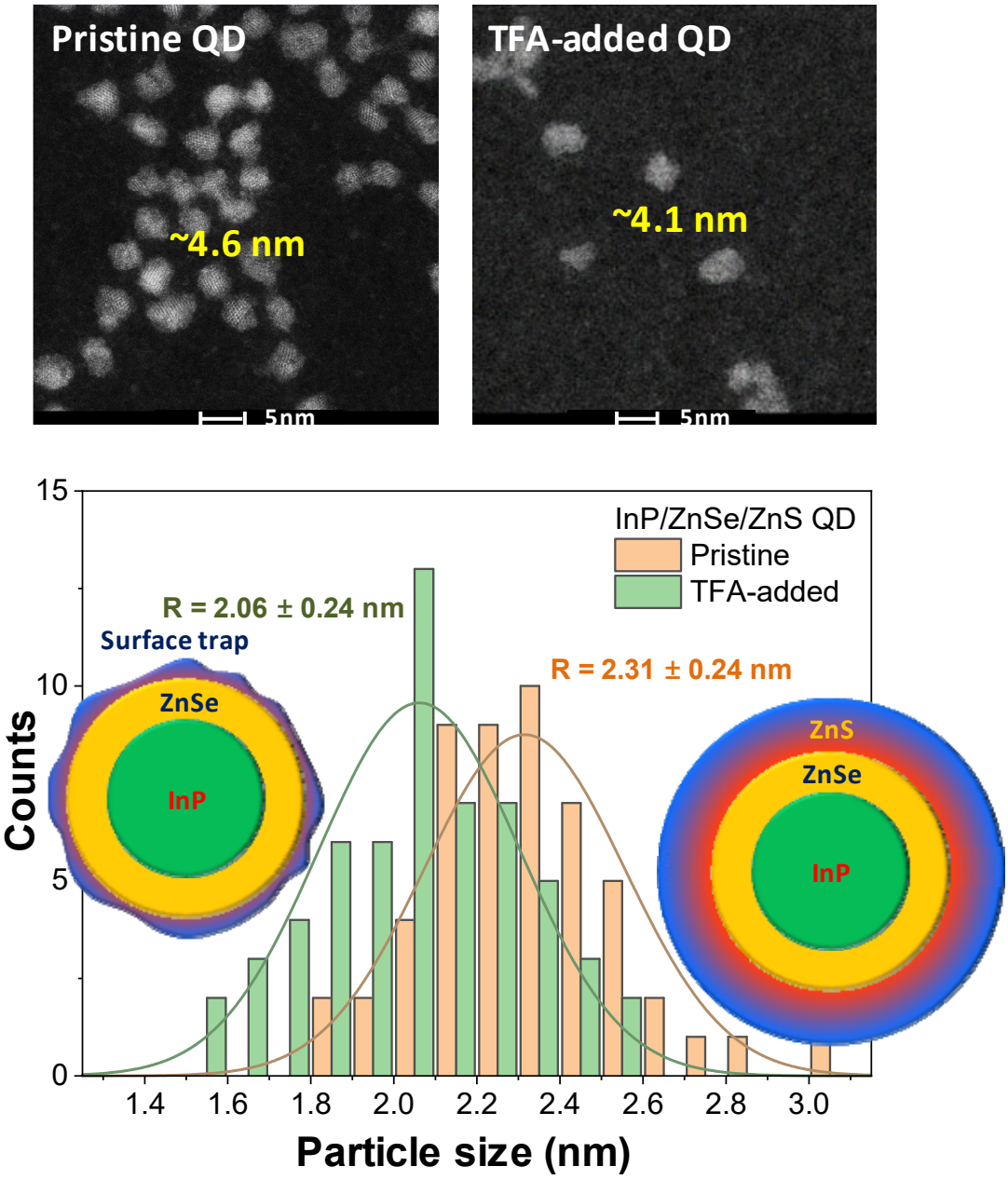

Figure S2. Transmission electron microscopy (TEM) images and size distribution of pristine and TFA-added quantum dots (QDs)

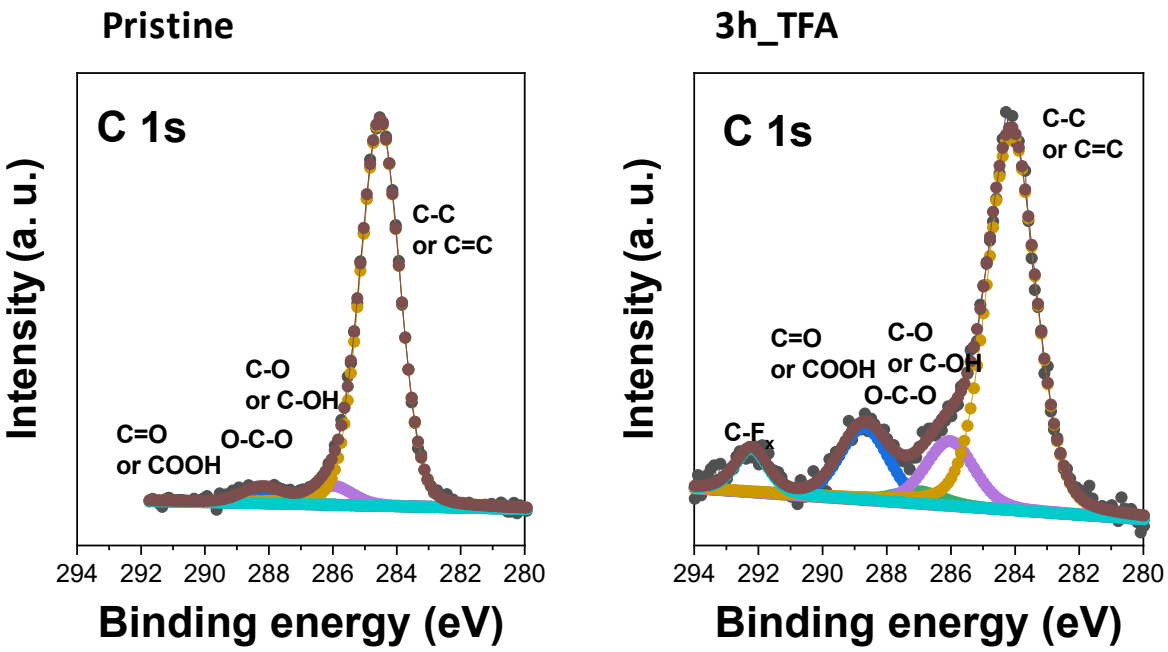

Figure S3. XPS results (C 1s) of pristine (left) and TFA-added (right) InP/ZnSe/ZnS quantum dots (QDs).

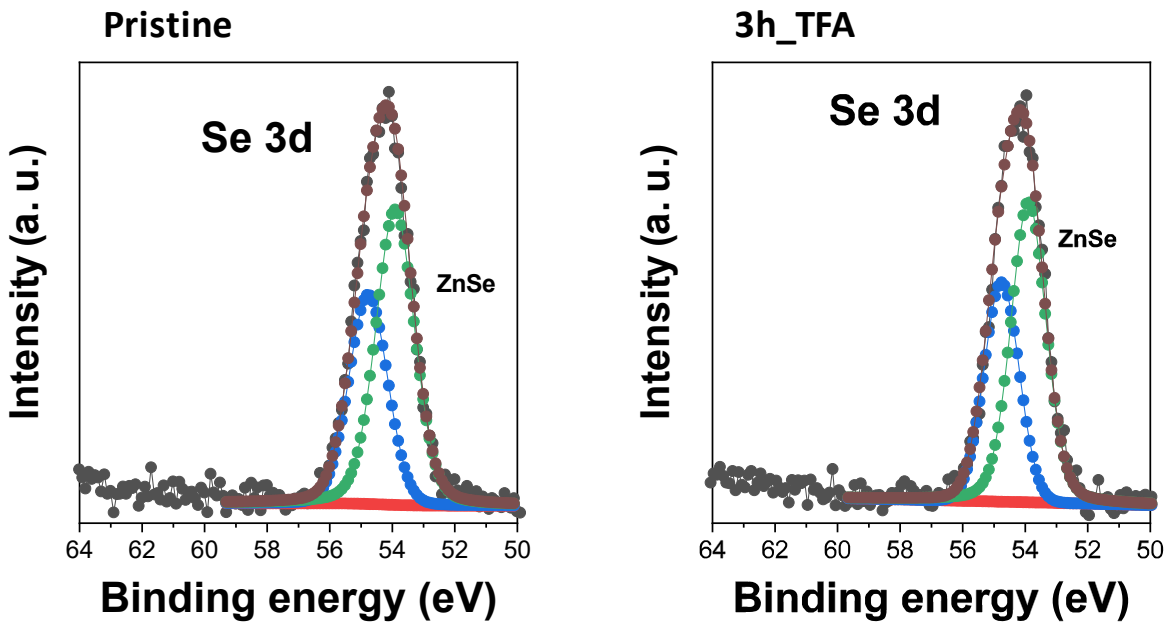

Figure S4. XPS results (Se 3d) of pristine (left) and TFA-added (right) InP/ZnSe/ZnS QDs having thin (top) and thick (bottom) ZnS shells. Concentration of oleic acid (OA) in the pristine and TFA-added InP/ZnSe/ZnS QDs.

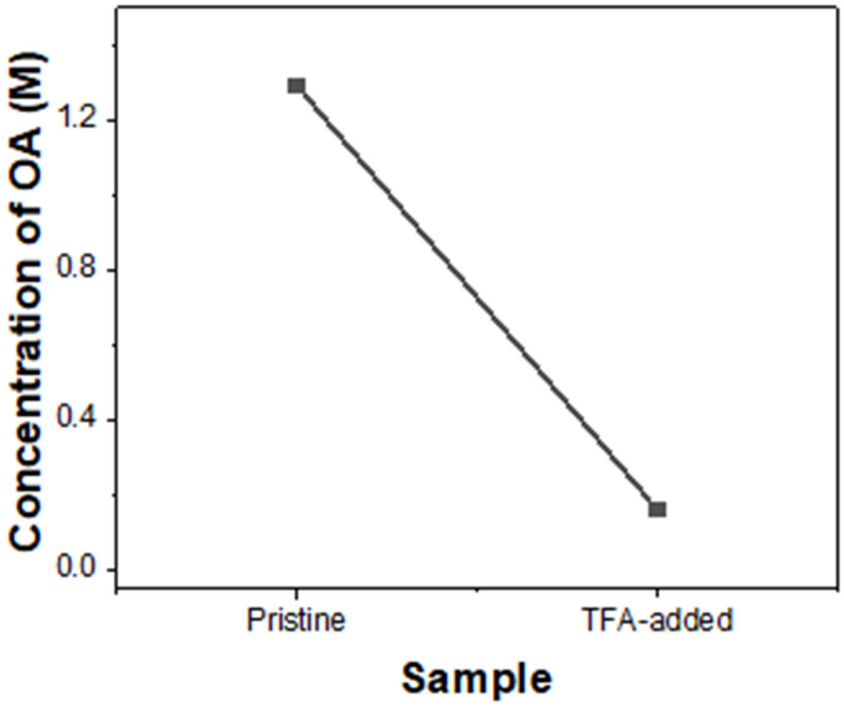

Figure S5. Concentration of oleic acid (OA) in the pristine and TFA-added InP/ZnSe/ZnS QDs.

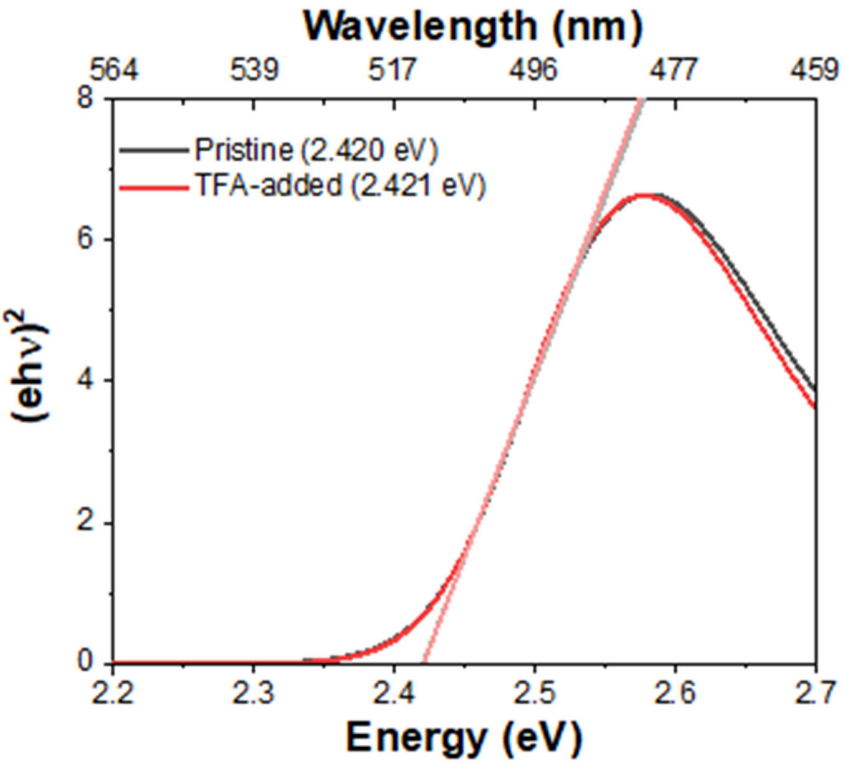

Figure S6. Tauc plots of pristine and TFA-added InP/ZnSe/ZnS QDs.

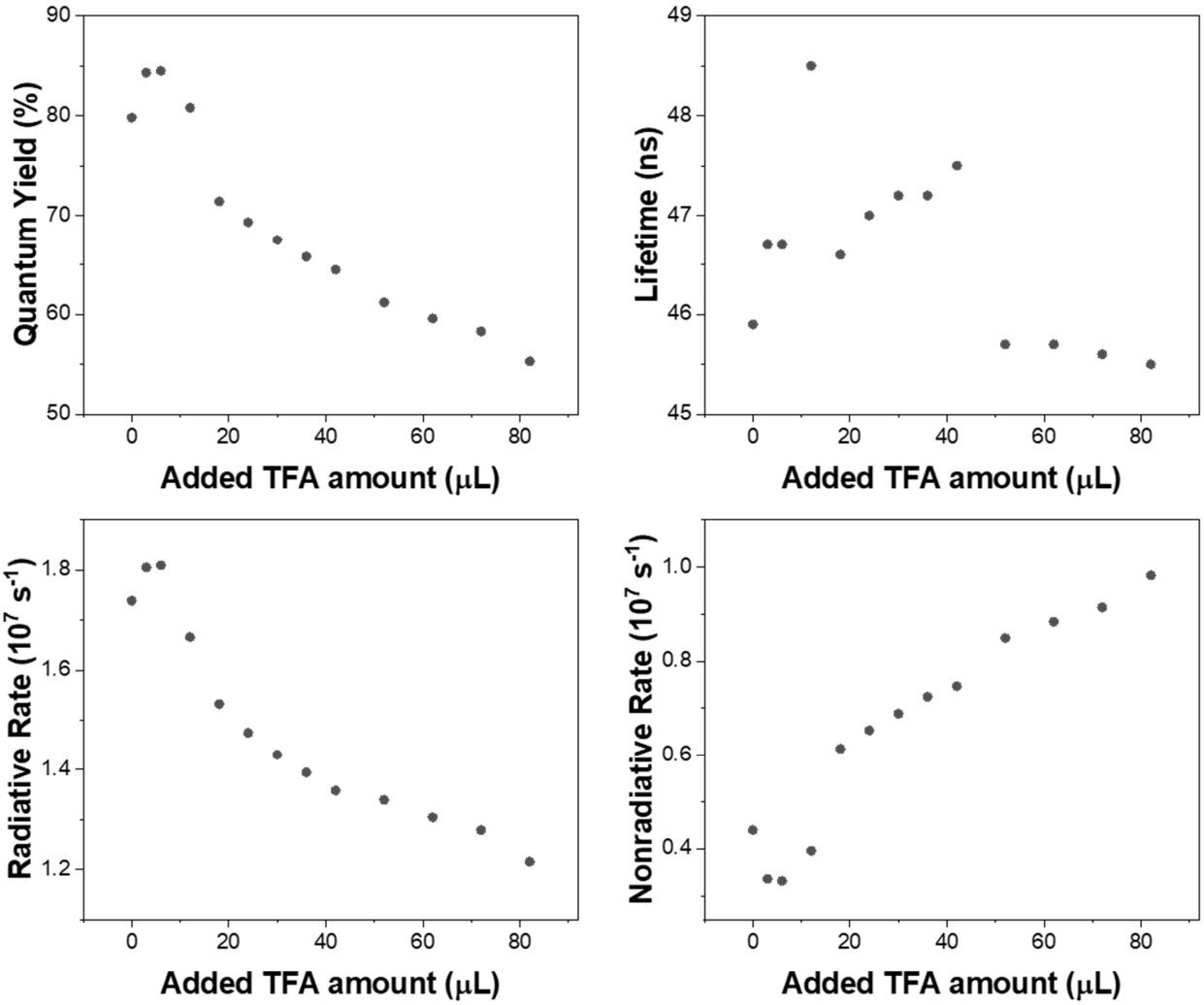

Figure S7. Quantum yields, lifetime, radiative and nonradiative rates of InP/ZnSe/ZnS QDs with increasing TFA amounts.

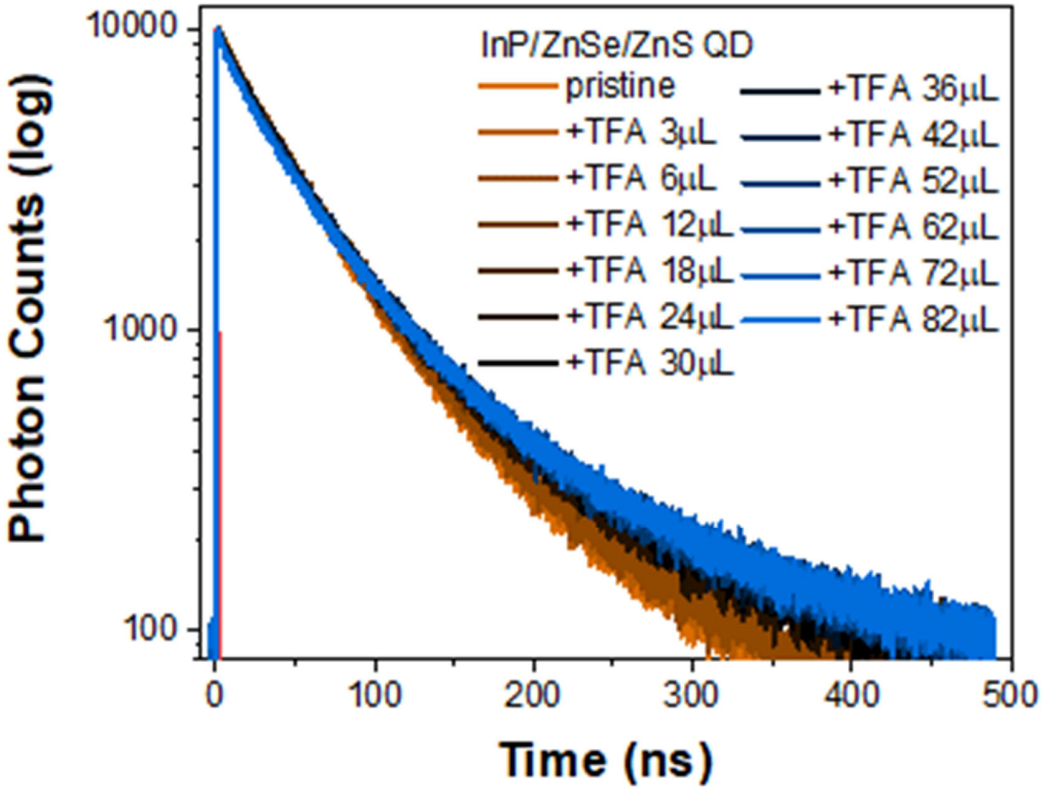

Figure S8. Time-resolved photoluminescence (TRPL) results of InP/ZnSe/ZnS QDs with increasing TFA amounts.

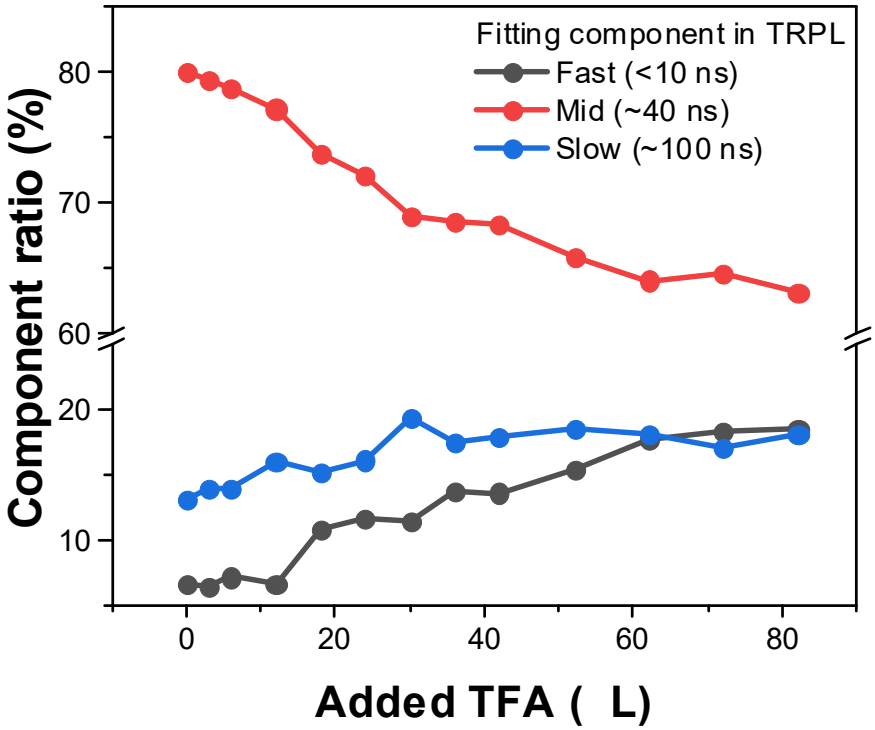

Figure S9. TRPL fitting component ratio of InP/ZnSe/ZnS QDs with increasing TFA amounts.

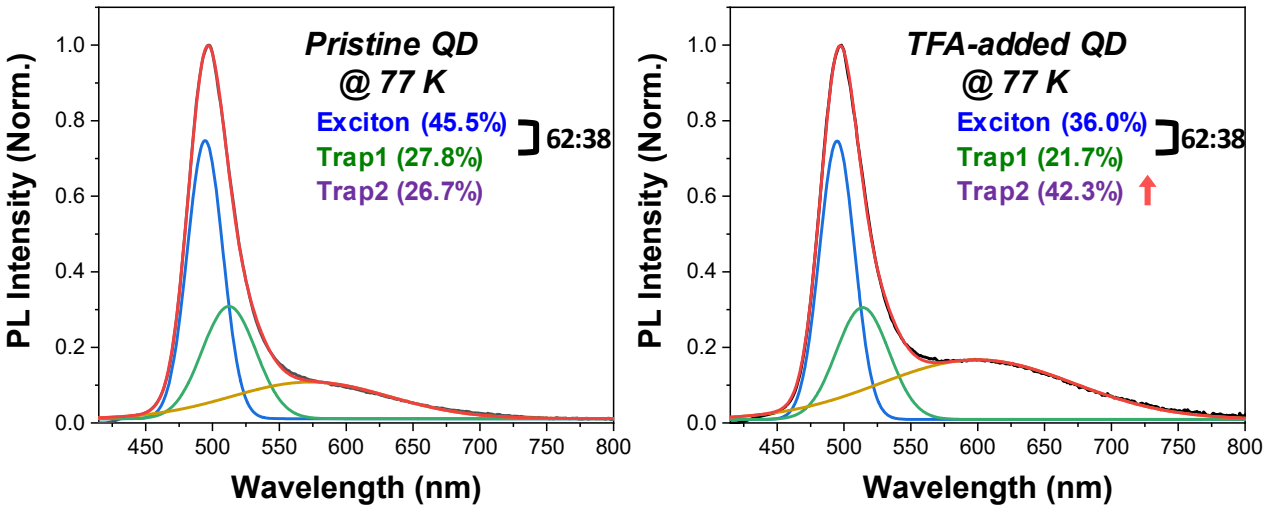

Figure S10. Fitted photoluminescence (PL) spectra of the pristine and TFA-added InP/ZnSe/ZnS QDs at 77 K.

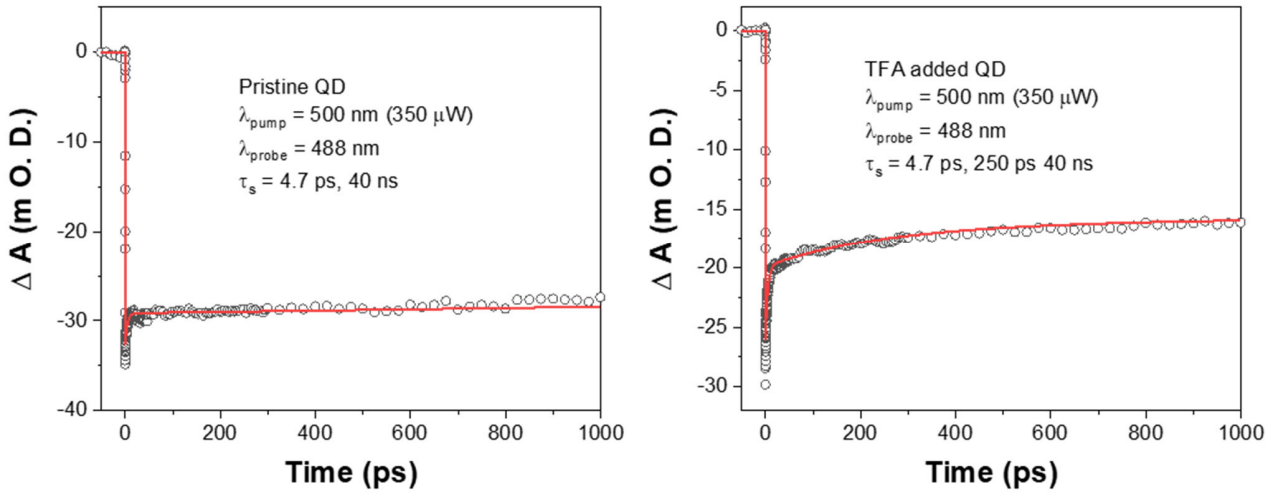

Figure S11. Decay profiles in the TA spectra of the pristine (left) and TFA-added (right) QDs.

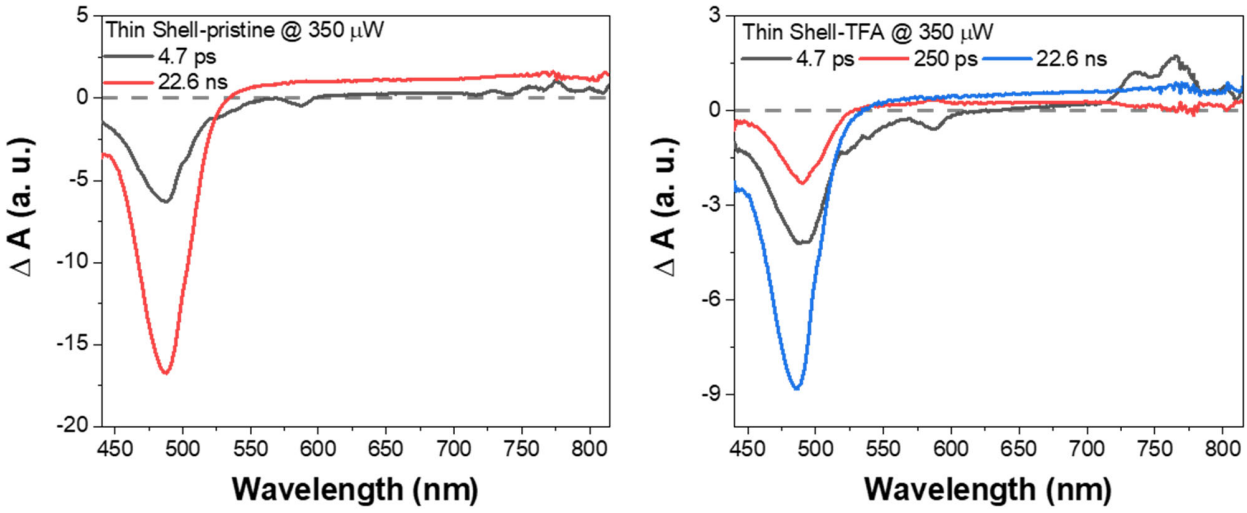

Figure S12. Decay associated (DA) spectra of the pristine (left) and TFA-added (right) QDs.

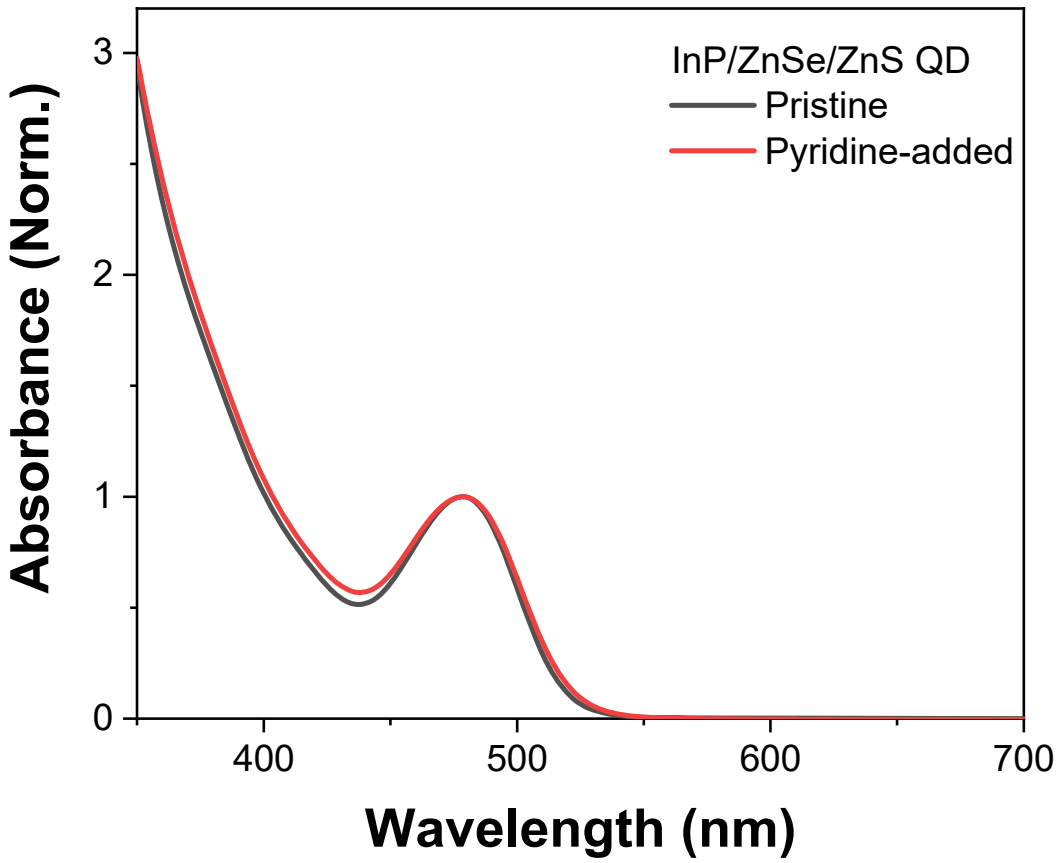

Figure S13. Absorption spectra of the pristine and pyridine-substituted InP/ZnSe/ZnS QDs.

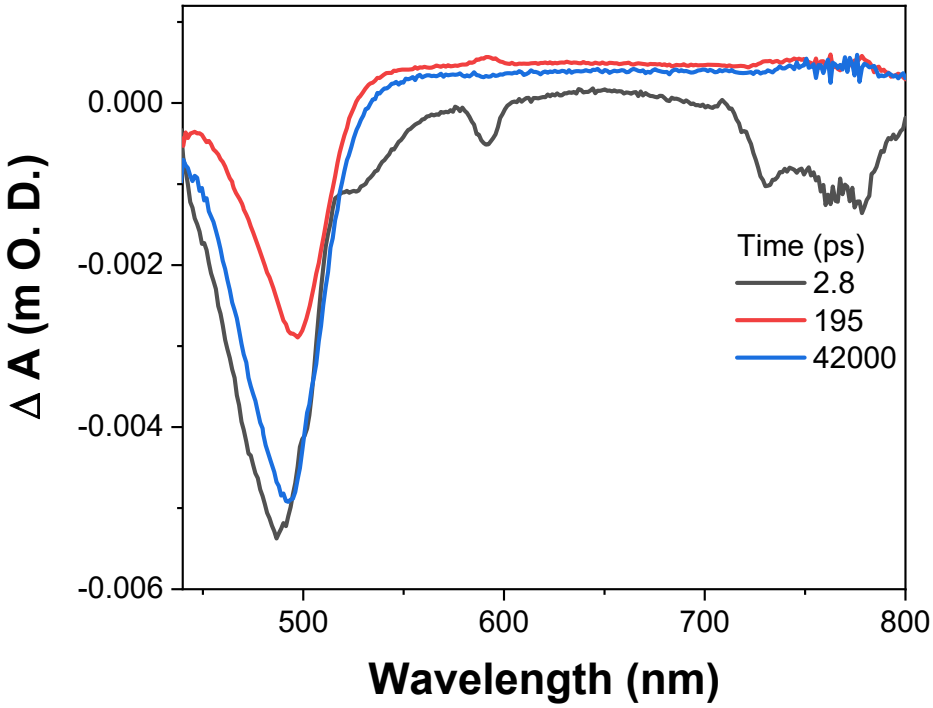

Figure S14. Decay associated (DA) spectra of the pyridine-treated QDs.

Table S1. XPS and ICP results of InP/ZnSe/ZnS QDs.

	XPS				ICP				
	Zn2p3	In3d5	Zn3d/In4d	Zn2p3/In3d5	P	S	Zn	Se	In
InP/ZnSe/ZnS QD	5.8	0.8	7.81	7.25	0.83	7.8	14.83	3.3	1

Table S2. Gas chromatography (GC) results of pristine and TFA-added InP/ZnSe/ZnS QDs

	OA	TFA
Pristine QD	0.77 M	-
TFA-added QD	0.05 M	0.18 M