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SUPPORTING INFORMATION

Indium-Based Quantum Dots Trapped in Solid-State Matrices: A One-Pot Synthesis, Thermoresponsive Properties, and Enhanced Micropollutant Removal

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Synthesis of colloidal Copper indium disulfide (CIS) and Zinc copper indium disulfide (ZCIS) QDs:

Synthesis of CIS QDs

The CIS and ZCIS QDs were synthesized through following a reported synthesis method [1]. CIS QDs were synthesized through a one-pot method by combining 0.4 mmol of CuI, 0.4 mmol of $In(CH_3COO)_3$, 0.4 mL of oleylamine, 2 mL of 1-dodecanethiol (DDT), and 2 mL of 1-octadecene (ODE). The reagents were mixed in a three-neck round-bottom flask under a nitrogen atmosphere. Subsequently, the mixture was subjected to heating at 120°C under a nitrogen atmosphere while being stirred magnetically for 1 hour. Following this, the temperature was raised to 230°C (the designated reaction temperature) and maintained for 15 minutes. The resultant pure copper indium disulfide quantum dots (CIS QDs) were promptly cooled to room temperature and then diluted to a final volume of 20 mL with octadecene. The solution was precipitated by addition of acetone to octadecene, and then dispersed in hexane.

Synthesis of ZCIS QDs

Zn precursor solution was synthesized by mixing 0.5 mmol Zinc stearate with 0.3 mL OA, 1.6 mL ODE, and 1 mL DDT in a three-neck round-bottom flask under nitrogen atmosphere. The mixture was magnetically stirred at 120°C in an inert atmosphere until it achieved optical transparency. Subsequently, the mixture was maintained at 120°C for later injection.

ZCIS QDs were synthesized by using one-pot synthesis method by mixing 0.4 mmol of CuI, 0.4 mmol of $In(CH_3COO)_3$, 0.4 mL of oleylamine, 2 mL of 1-dodecanethiol (DDT), and 2 mL of 1-octadecene (ODE) at 120°C for 30 minutes under a nitrogen atmosphere. Following this, the temperature was raised to 230°C, and the Zn precursor solution was continuously injected into the ZCIS solution through a syringe pump, immediately) and maintained for 30 minutes. The solution was finally cooled to room temperature, precipitated by addition of acetone to octadecene, and then dispersed in hexane. Same procedure was repeated to synthesize colloidal ZCIS QDs by replacing DDT with thioacetamide.

Properties of colloidal CIS and ZCIS QDs

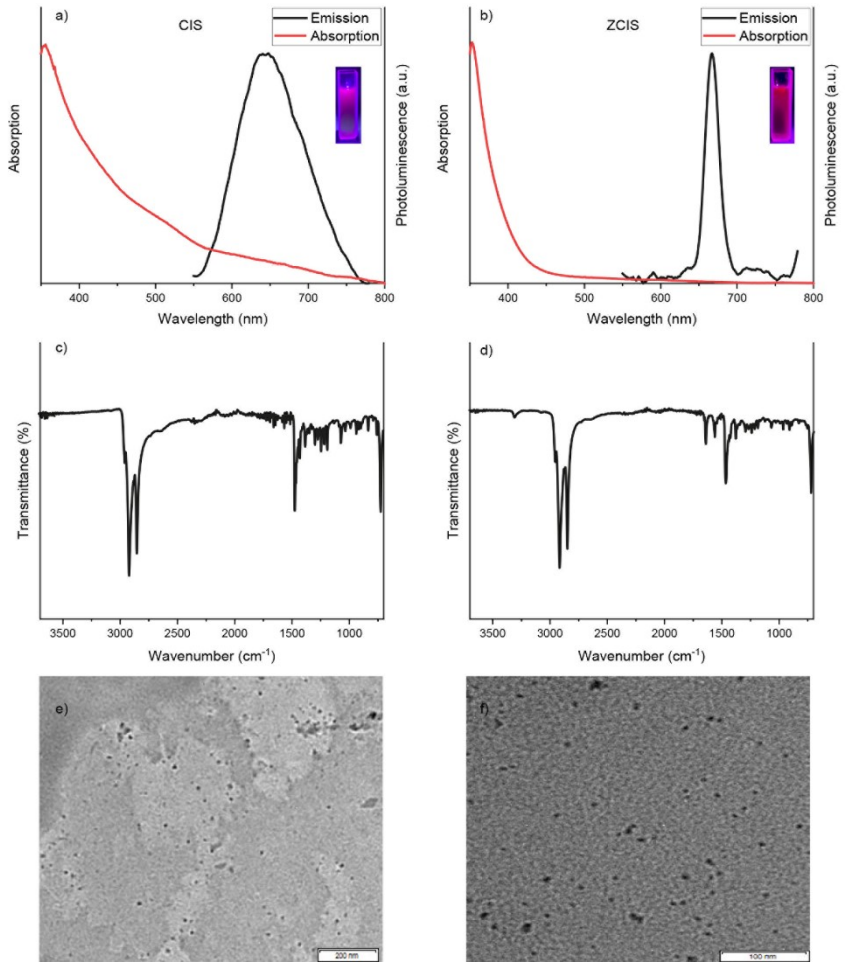

Figure 1. Absorption and photoluminescence spectrum of **a)** colloidal CIS QDs, **b)** colloidal ZCIS QDs. FTIR spectra of **c)** colloidal CIS QDs, **d)** colloidal ZCIS QDs. TEM image of **e)** colloidal CIS QDs, **f)** colloidal ZCIS QDs. QDs were excited at 400 nm. The inset fluorescence pictures were taken under 366 nm UV-light.

In our study, colloidal CuInS (CIS) and ZnCuInS (ZCIS) QDs were initially synthesized following the literature without any modifications in order to compare the properties of QDs in colloidal form and SSQDs [1]. The colloidal CIS and ZCIS QDs which were synthesized in this study exhibited structural and photophysical properties similar to those reported previously [1]. The colloidal QDs had typical broad absorption spectrum and an emission peak at approximately 645 nm for CIS QDs and 665 nm for ZCIS QDs (Figure S1). The photoluminescence quantum yield of CIS QDs calculated to be 7.2%, while the photoluminescence quantum yield of ZCIS QDs found to be 13.4%. Additionally, the Fourier-transform infrared (FTIR) spectroscopy of the QDs indicated that the capping agent, oleylamine, bound to the QDs through amine groups, leaving long carbon chains free, which

made them hydropobic colloidal nanomaterials (Figure S1). The transmission electron microscopy (TEM) results revealed that the QDs were monodisperse with average size of approximately 5 nm for CIS QDs and 6 nm for ZCIS QDs (Figure S1). All these results were consistent with what was previously observed in the literature [1].

The size distribution of SSQDs

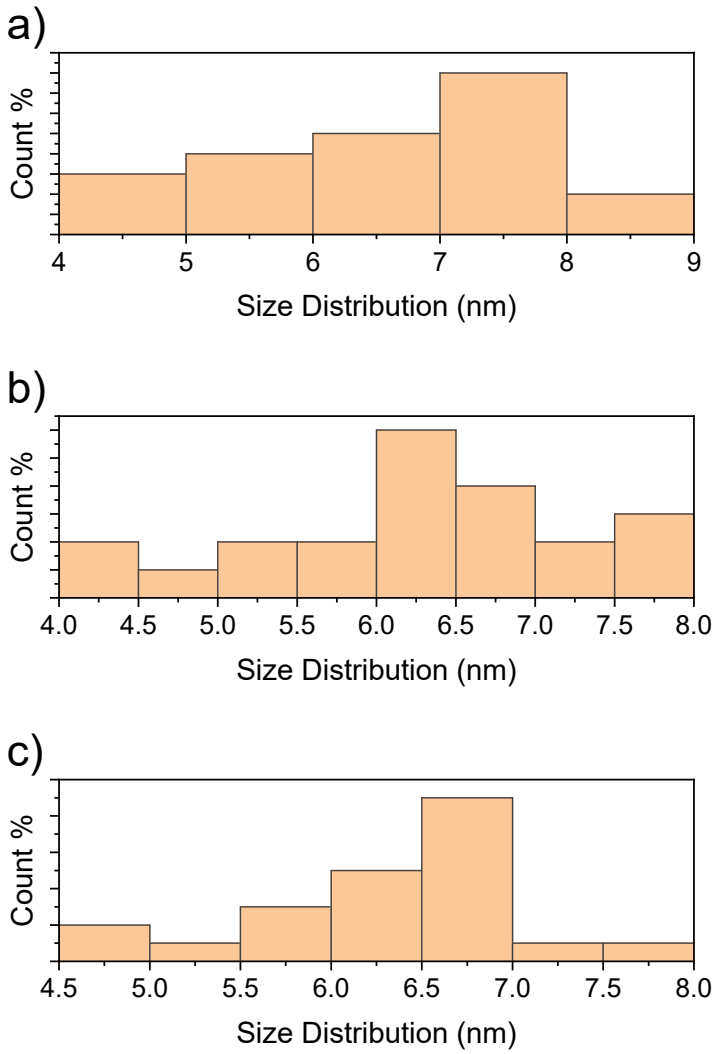

Figure S2. Size distribution of a) In_2S_3, b) $ZnIn_2S_4$ and c) $Cu:ZnIn_2S_4$ SSQDs.

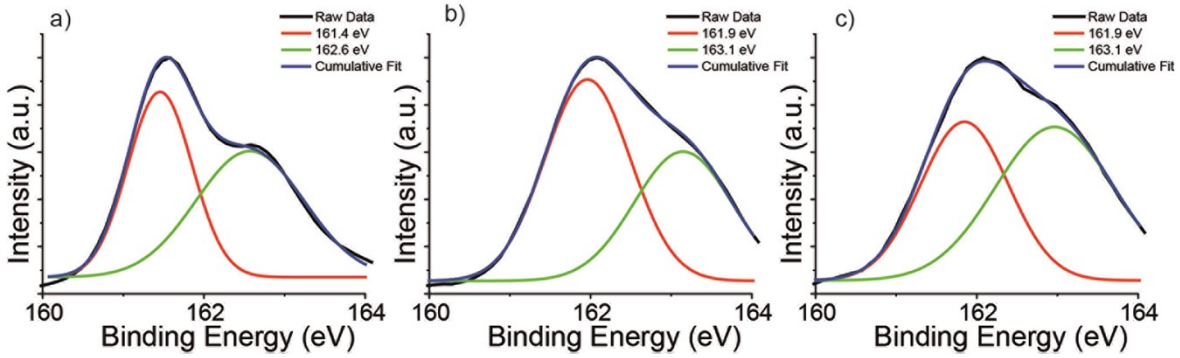

Figure S3. HR-XPS spectrum of S(2p) of a) In_2S_3, b) $ZnIn_2S_4$ and c) Cu:$ZnIn_2S_4$ SSQDs.

FTIR spectra of SSQDs

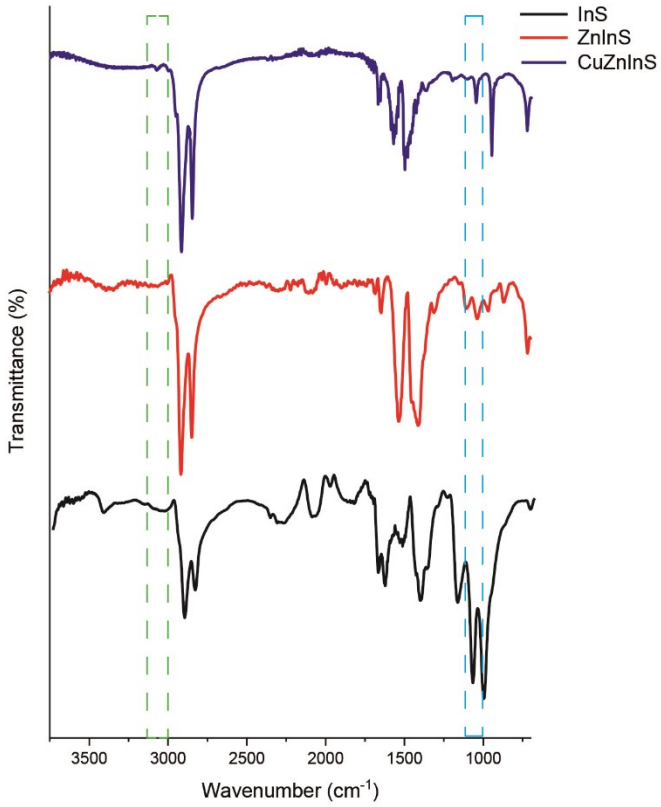

Figure S4. FTIR spectra of In_2S_3, $ZnIn_2S_4$ and Cu:$ZnIn_2S_4$ SSQDs. The blue box is for 1000 – 1100 cm^{-1}. The green box is for 3000 – 3100 cm^{-1}.

***Synthesis of CdSeS quantum dots*:**

The CdSeS quantum dots were synthesized by following method; The synthesis of CdSSe quantum dots began by dissolving 0.2 g of Cadmium Myristate (as the Cadmium precursor) and 1.50 g of Oleic Acid (5.3 mmol) in 50 mL of toluene under a nitrogen atmosphere at 90 °C until a clear solution was achieved. Next, in a 250 mL three-necked round-bottom reaction flask, 60 mg of thiourea (0.79 mmol, sulfur precursor) and 2 mL of freshly prepared NaHSe solution were dissolved in 40 mL of distilled water at 100 °C and refluxed under a nitrogen atmosphere. Subsequently, the cadmium myristate – oleic acid solution was added to the aqueous NaHSe-Thiourea solution. The cations and anions began to interact at the interface of the two phases (toluene-water), forming quantum dots in the toluene phase. The reaction temperature was maintained at 100 °C for the growth of quantum dots until the desired size was achieved. The reaction was halted at 24 hours by cooling down the reaction mixture. Afterward, the toluene and water phases were separated, and the toluene phase was filtered. All steps were conducted under a nitrogen atmosphere. Finally, the quantum dots were obtained by precipitation with methanol. The resulting quantum dots were air-stable and stored in the same solution at 2–8 °C in the refrigerator.

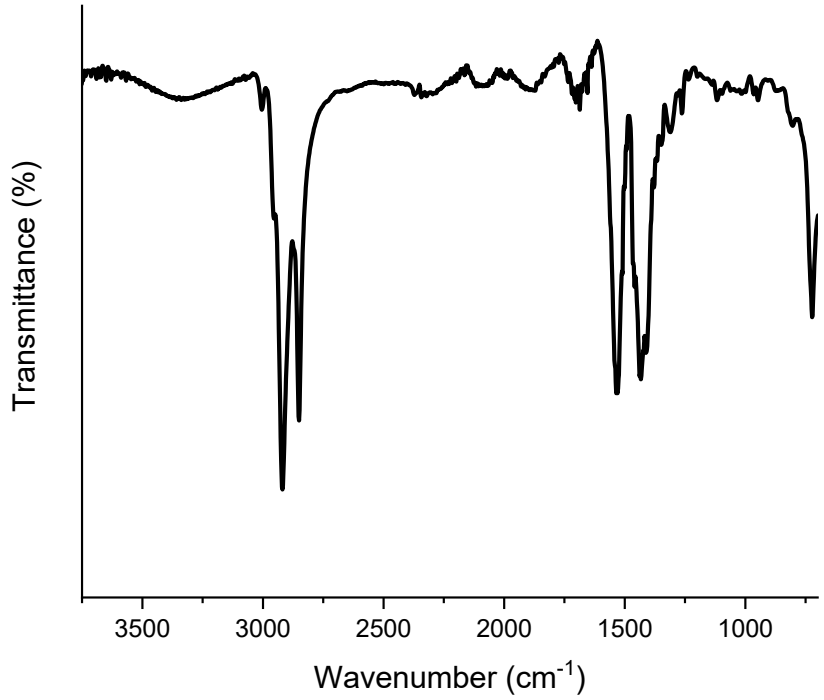

Figure S5. Fourier Transformed Infrared spectrum of oleic acid capped CdSeS QDs.

Fluorescence Quantum Yields of SSQDs

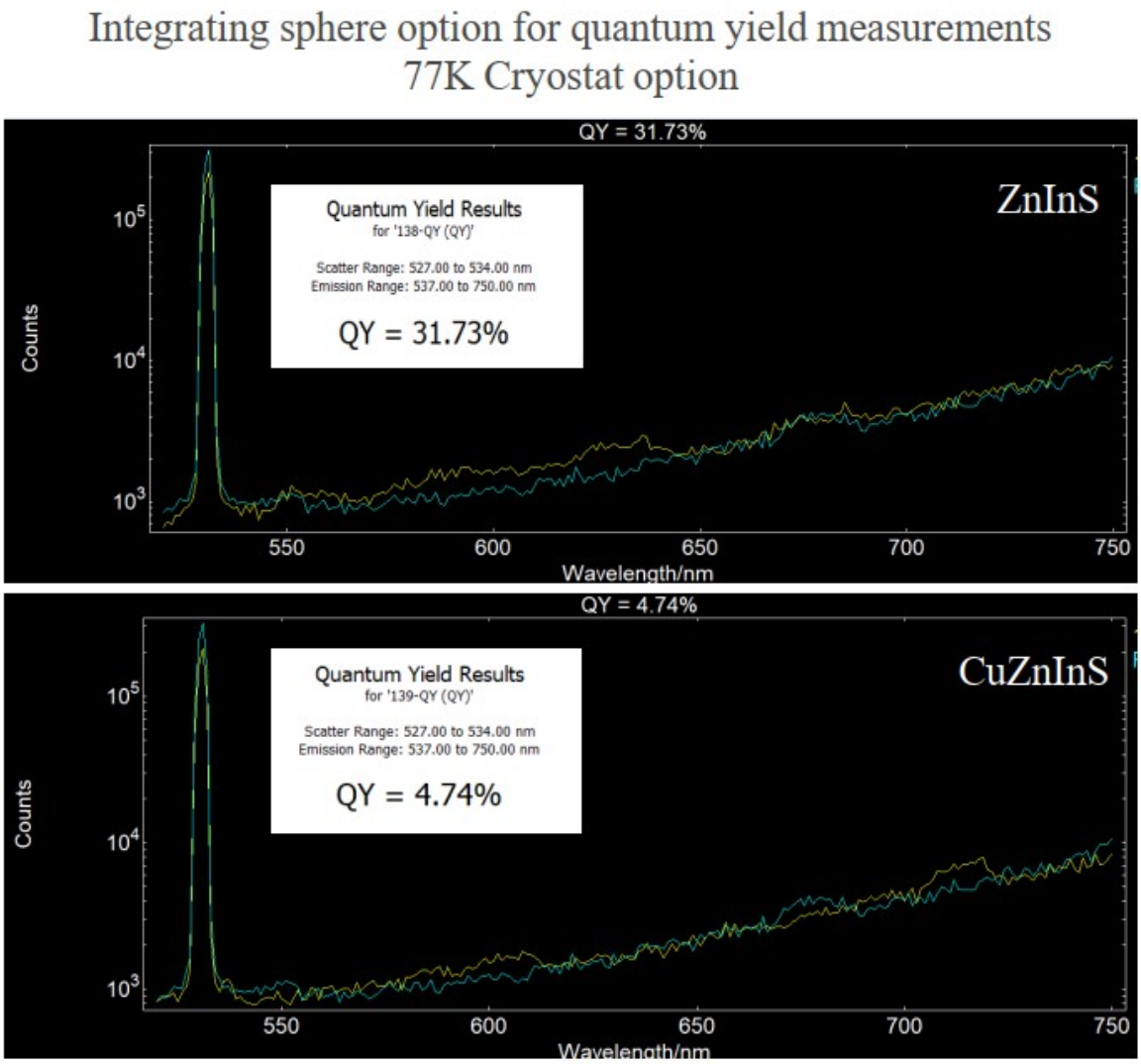

Figure S6. The results of measurement of fluorescence quantum yield (QY) of $ZnIn_2S_4$ and Cu:$ZnIn_2S_4$ SSQDs. It should be noted that the QY of In_2S_3 SSQDs was below 1%, so the measurement was not included in here.

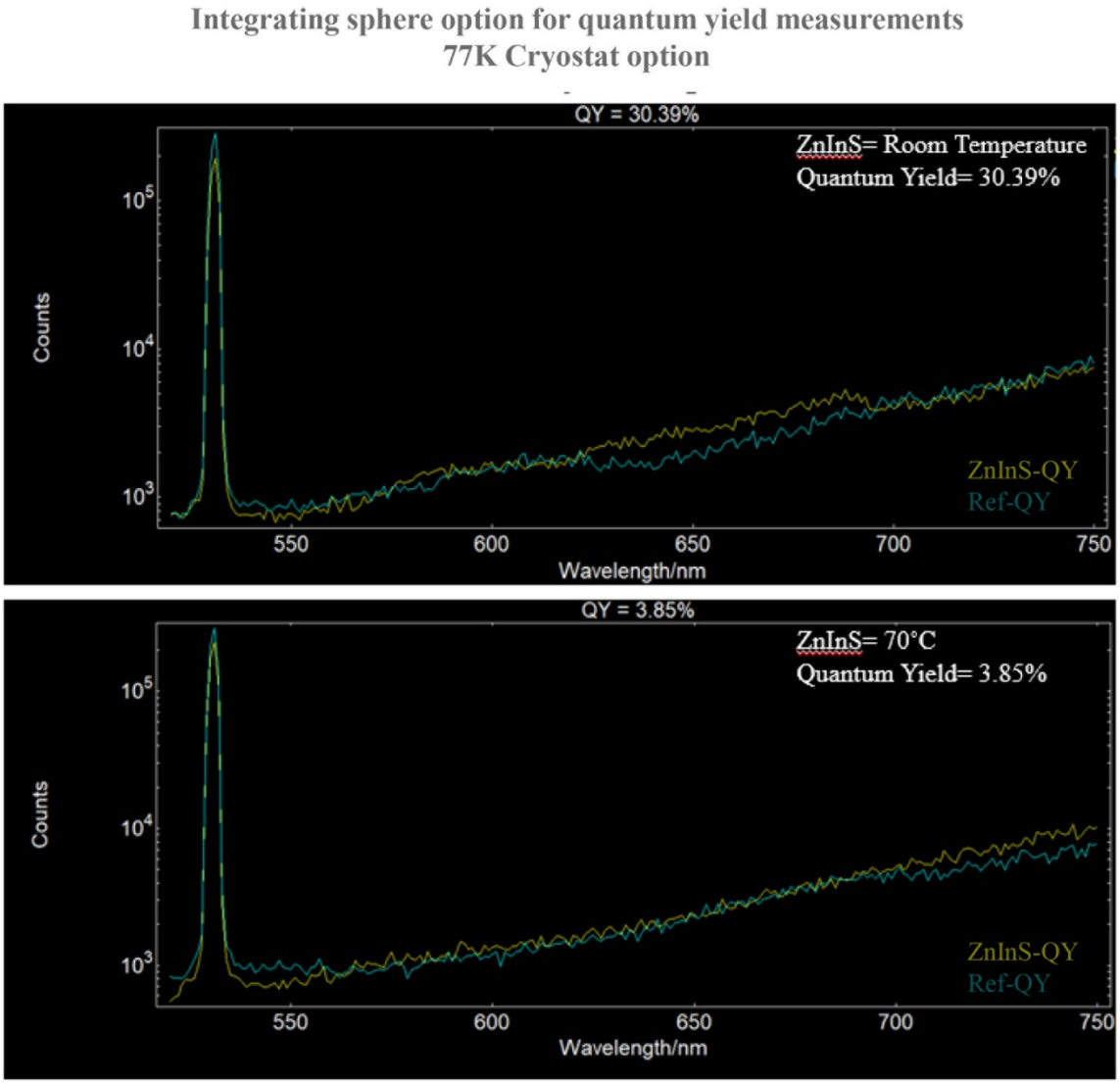

Figure S7. The change in quantum yield of SSQD upon heating. The quantum yield of the SSQD dropped to 3% at 80°C.

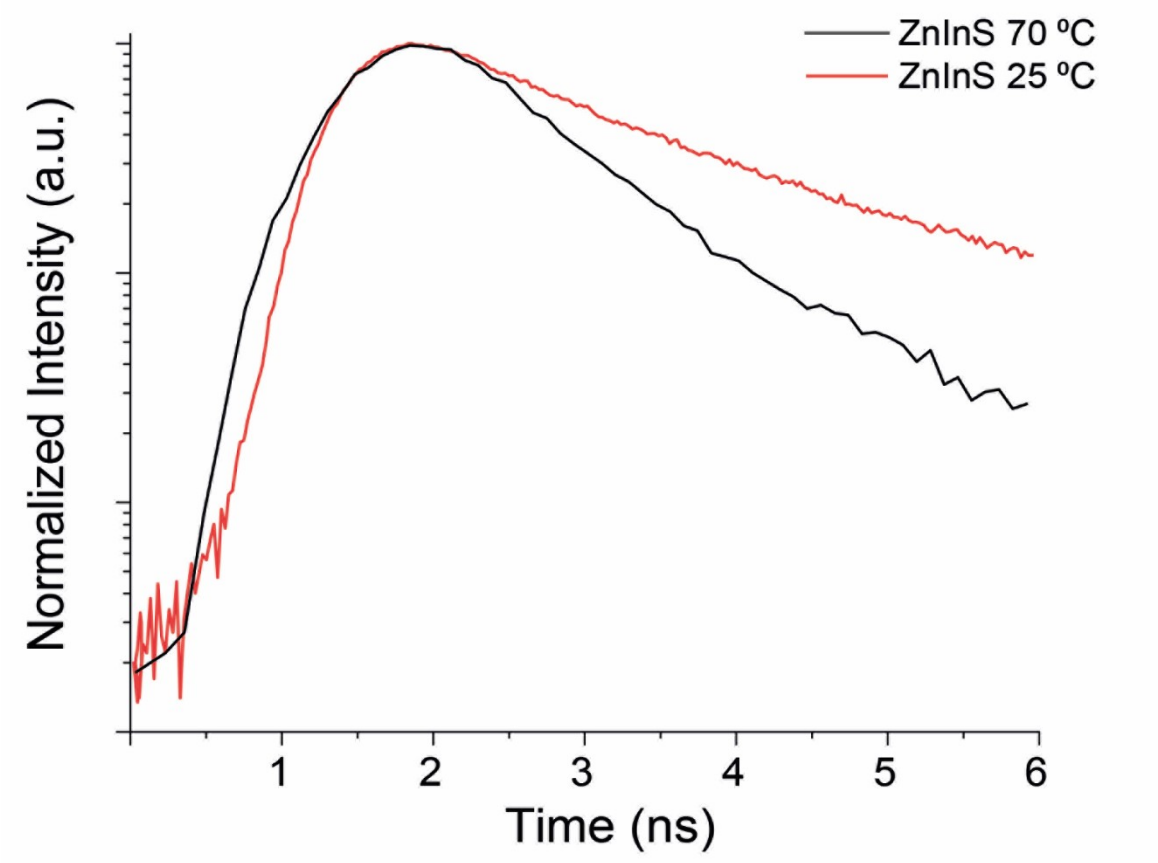

Figure S8. The change in fluorescence kinetics of SSQD upon heating. The fluorescence kinetics of the SSQD became faster at 70°C due to formation of a fast decay component.

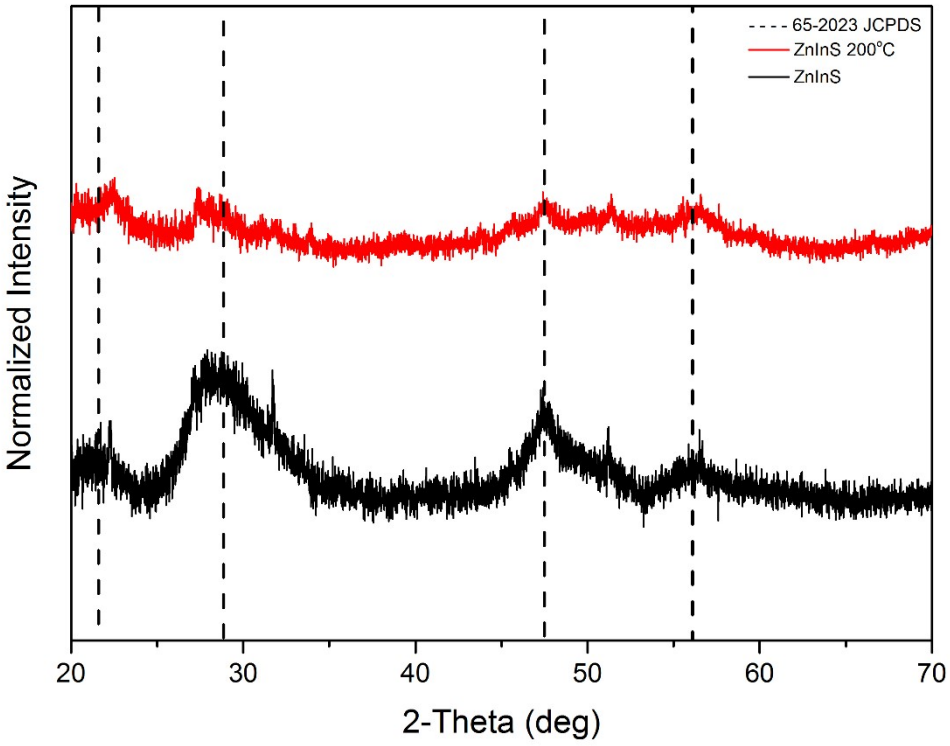

Figure S9. XRD spectra of $ZnIn_2S_4$ SSQDs treated at 200°C for 5 minutes and remained at room temperature (ZnInS represents $ZnIn_2S_4$).

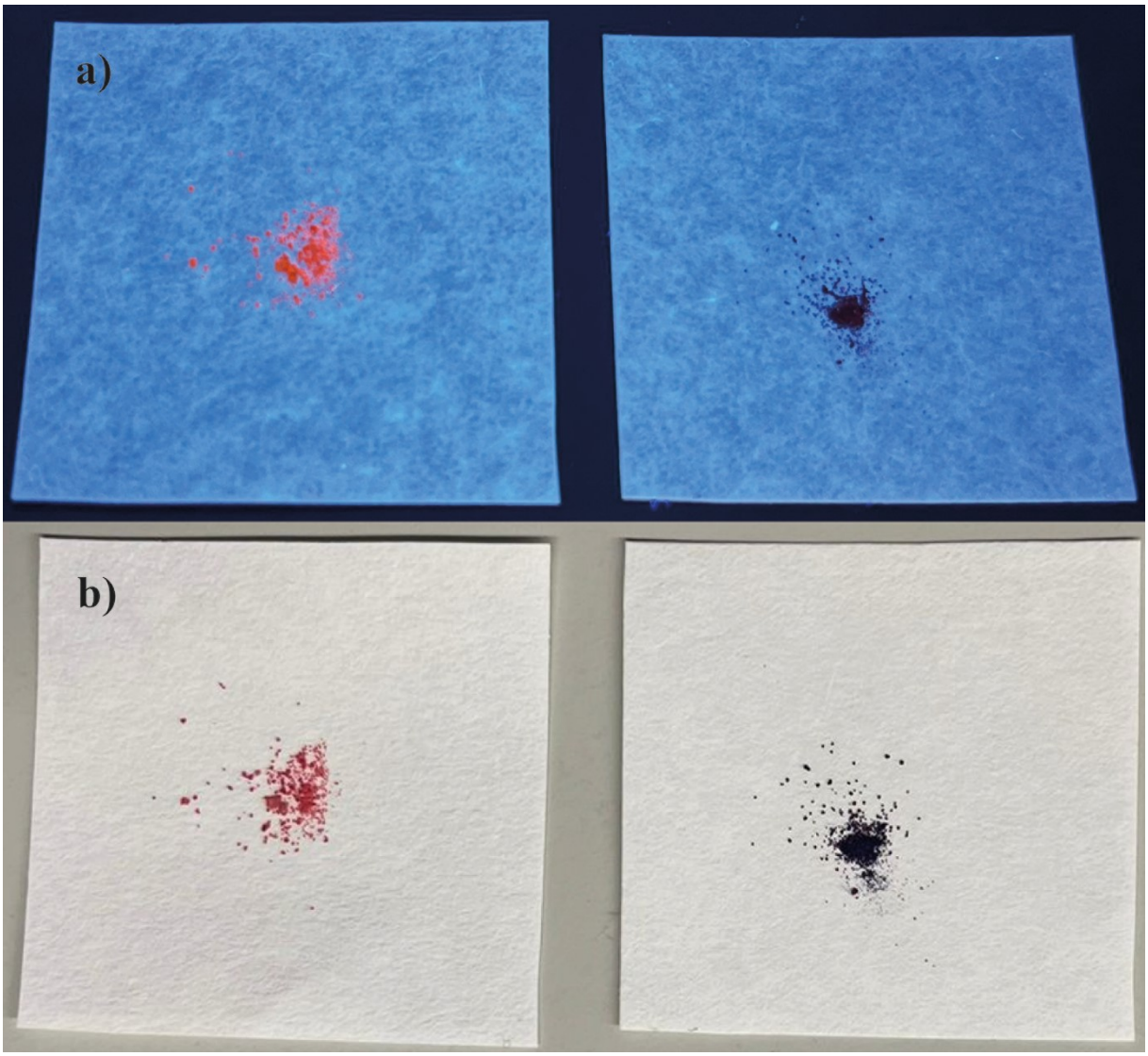

Figure S10. The fluorescence quenching of SSQD ($ZnInS_2$) upon adsorption treatment with methyl violet. a) under UV light (366 nm) b) under day light. On the left before adsorption on the right after adsorption.

REFERENCES

1 M. Zhu, Y. Li, S. Tian, Y. Xie, X. Zhao and X. Gong, *J. Colloid Interface Sci.*, , DOI:10.1016/j.jcis.2018.09.065.