

Supporting Information

Quaternary Zn-Ag-In-Se Quantum Dots for Biomedical Optical Imaging of RGD-Modified Micelles

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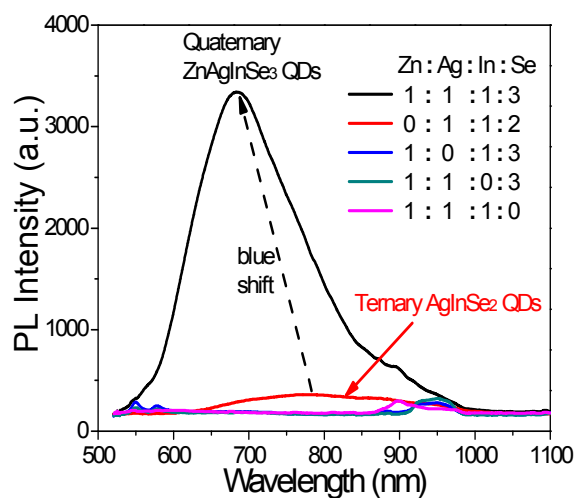


Figure S1. Photoluminescence (PL) spectra of the dispersions prepared with different Zn/Ag/In/Se feed ratios, in which Se powder dissolved in the mixture of oleylamine (OLA) and 1-dodecanethiol (DDT) was used as Se source (selenium can be reduced by DDT, and further associates with OLA to form the OLA–Se complexes¹). In this quaternary system, the absence of Zn from the reaction mixture results in a significant decrease in PL intensity of QDs, whereas in the absence of any one of In, Ag and Se, no PL emission is observed. This indicates that the host QDs should be composed of an alloy of Zn, Ag, In and Se, namely, the

formation of quaternary ZnAgInSe_3 QDs. And as compared with ternary AgInSe_2 QDs ($\lambda_{\text{em}} \sim 800$ nm), the PL peak ($\lambda_{\text{em}} = 685$ nm) of the QDs formed in the quaternary system blue-shift greatly, which further confirms the formation of quaternary ZAISe QDs (the band gaps of bulk AgInSe_2 and ZnSe are 1.24 and 2.7 eV, respectively^{2,3}).

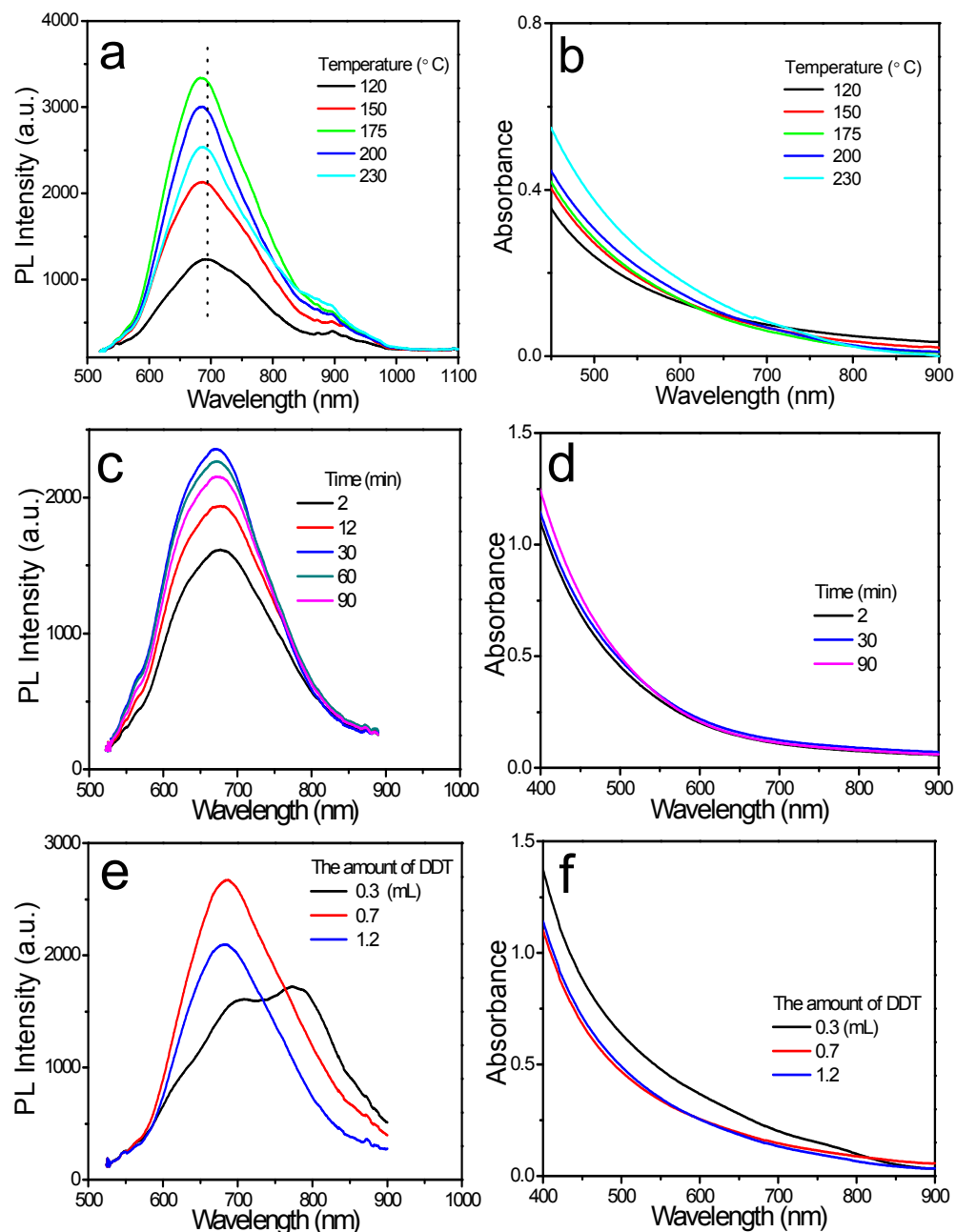


Figure S2. (a) PL and (b) absorption spectra of quaternary ZAISe QDs synthesized during a programmed heating process from 120 to 230 °C (rate: ~ 3 °C/min). Temporal evolutions of (c) PL and (d) absorption spectra of quaternary ZAISe QDs synthesized at 175 °C. (e) PL and (f) absorption spectra of quaternary ZAISe QDs prepared by varying the amount of DDT.

Effect of Reaction Temperature: Figures S2a and S2b show the PL and absorption spectra of the quaternary ZAISe QDs prepared at different reaction temperatures during a programmed heating process respectively, in which the Zn/Ag/In/Se feed ratio was set to 1:1:1:3. As shown, with increasing the reaction temperature from 120 to 230 °C, the overall PL intensity initially became stronger, and then, reached the maximum at 175 °C, while further increasing the temperature would cause a gradually decrease in PL intensity. Noting that with the increase of the reaction temperature, PL peak position only blue shifted several nanometers, which indicated that in this synthesis, by controlling the reaction temperature, quaternary ZAISe QDs with wide tunable PL emission could not be prepared. In addition, these data also indicate that the OLA–Se complexes formed by dissolving Se powder in the mixture of OLA and DDT are highly reactive. It is found that even at 90 °C, the OLA–Se complexes can react with Zn^{2+} , Ag^+ and In^{3+} to form quaternary ZAISe QDs.

Effect of Reaction Time: The temporal evolutions of both PL and absorption spectra of the quaternary ZAISe QDs during the synthesis at 175 °C are shown in Figures S2c and S2d, respectively. As shown, the reaction time of 30 min is favorable for achieving the highest PL intensity for the quaternary ZAISe QDs. In addition, with prolonging reaction time (from 2 to 90 min), no obvious blue-shift in the PL peak of QDs is observed, and the absorption spectra of the quaternary QDs were almost kept constant from the starting point-injection of the selenium precursor solution. Furthermore, the size of QDs was almost unchanged with increased reaction time. These experimental results suggest that homogeneous quaternary ZAISe nuclei with certain compositions are formed directly by the reaction between cations and selenium due to the assistance of the cation reactivity-controlling ligand–DDT.⁴

Effect of Amount of DDT: Figures S2e and S2f show the PL and absorption spectra of the quaternary ZAISe QDs prepared by varying the amount of DDT (dodecanethiol), respectively. As shown, the PL properties, e.g., the PL intensity and PL peak position of the resulting quaternary ZAISe QDs were found to strongly depend on the amount of DDT. Here, DDT is the reactivity-controlling ligand for cationic precursors (Ag and In), since the silver and indium had higher reactivity than zinc in the reaction with selenium in this synthesis system.⁵ Hence, decreasing the amount of DDT will result in the corresponding increase of the relative content of Ag^+ (and In^{3+}) constituent in quaternary ZAISe QDs. As a result, a concomitant red-shift in the PL peak was observed, since the band gap of Ag–Se (or Ag–In–Se) is low.² In addition, we noted that (i) the magnitude of the red-shift (~90 nm, from 680 to 770 nm) is small than that (~140 nm, from 660 to 800 nm) achieved by tuning the Ag/Zn feed ratio; (ii) decreasing the amount of DDT from 0.7 to 0.3 mL will induce a decrease in the storage stability of the resultant quaternary ZAISe QDs. Therefore, in this study, major efforts were focused on investigating and revealing the important role of the Ag/Zn feed ratio for the synthesis of the quaternary ZAISe QDs.

Finally, the reaction temperature of 175 °C, the reaction time of 30 min and the DDT amount of 0.7 mL (i.e., 0.5+0.2) have been proven to be optimal for achieving the highly luminescent quaternary ZAISe QDs. The spectral shifts induced by the change of the Ag/Zn feed ratio should be mainly attributed to the resultant variation in the composition of the QDs. That is, by introducing Zn ions, quaternary ZAISe alloyed QDs would be formed *via* alloying the wider band gap ZnSe (2.7 eV) with a narrower band gap AgInSe₂ (1.24 eV). And the bandgap

of ZAISE QDs will be larger with more Zn ions introduced (i.e., the increase of Zn content in the QDs). This result further enriches our understanding of the QD synthesis that different from binary QDs, for quaternary Zn–I–III–VI semiconductors QDs, their compositions might play a more important role in determining the PL peak position.

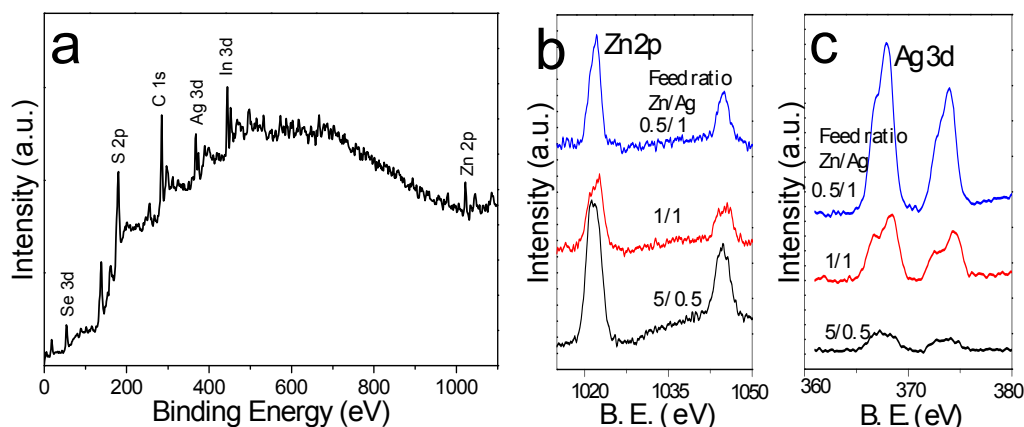


Figure S3. (a) XPS (X-ray photoelectron spectroscopy) survey spectrum of quaternary ZAISE QDs, (b) XPS spectra of Zn 2p of quaternary ZAISE QDs prepared with various Ag/Zn feed ratios and (c) the corresponding XPS spectra of Ag 3d.

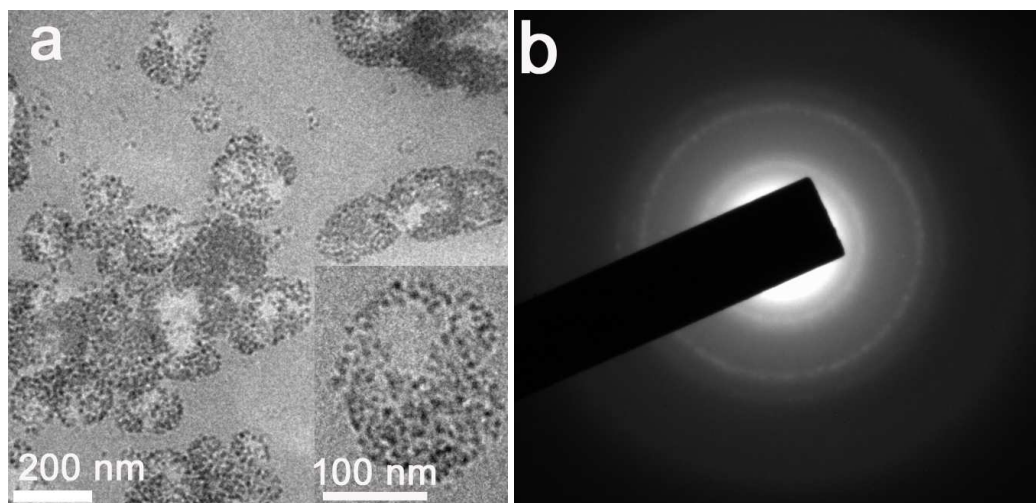


Figure S4. Typical TEM image (a) and the corresponding selected area electron diffraction (SAED) pattern (b) of the as-prepared QDs-loaded micelles. Inset: TEM image of a QDs/micelle nanocomposite. These data indicate that based on the hydrophobic interaction between the octyl groups of micelle and the dodecanethiol molecules on the QD surface (as schemed in Figure 1a), the oil-soluble QDs could be uploaded spontaneously into the micelles (achieving the phase transfer of oil-soluble QDs into water), while the size (~5 nm in diameter), morphology and crystal structure of the oil-soluble quaternary ZAISE QDs were retained.

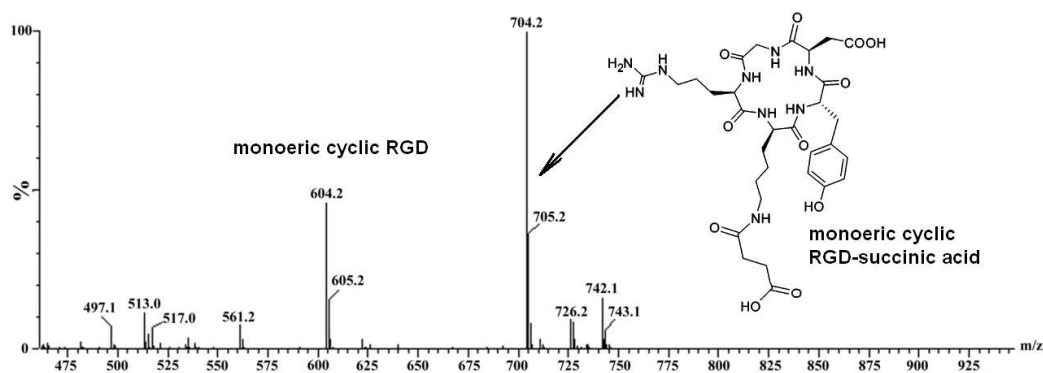


Figure S5. The mass spectrum of monoeric cyclic RGD-succinic acid prepared from the reaction between monoeric cyclic RGD and succinic anhydride. Inset, the structure of monoeric cyclic RGD-succinic acid.

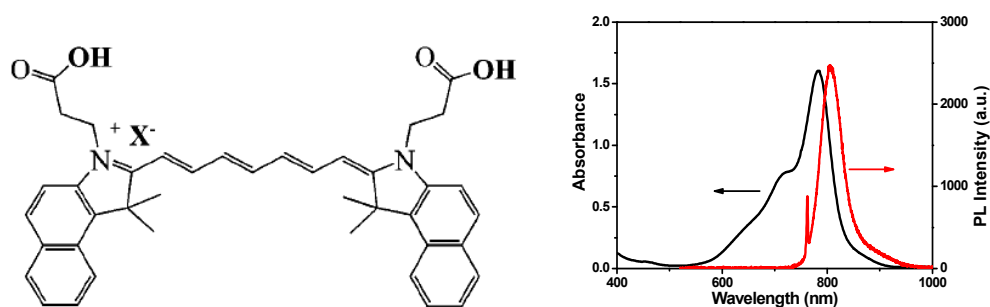


Figure S6. Left: The molecular structure of the NIR dye-cypate provided by prof. Samuel Achilefu.⁶ Right: Absorption and PL spectra of cypate.

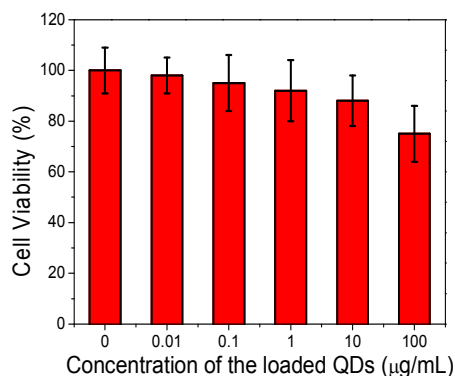


Figure S7. Cell viability of human embryonic lung fibroblast (HELFL) cells incubated with different concentrations of QDs-loaded RGD-SOC micelles ([QDs]=0, 0.01, 0.1, 1, 10, and 100 μg/mL) for 48 h. Here, MTT assay was conducted to assess preliminarily the cytotoxicity of QDs-loaded Micelles. The OD was measured with a Microplate Reader (Biorad).

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