Electronic supplementary information

Highly luminescent water-soluble quaternary Zn-Ag-In-S quantum dots for tumor cell-targeted imaging

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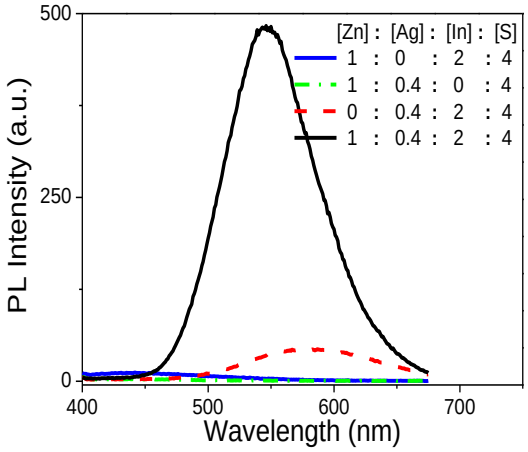

Fig. S1 Photoluminescence (PL) spectra of the dispersions prepared with different Zn/Ag/In/S ratios, where the thioacetamide (TAA) was used as S source. In this quaternary system, the absence of Zn from the reaction mixture results in a significant decrease in PL intensity of QDs, whereas in the absence of any one of In, Ag and S, no PL emission is observed. This indicates that the host QDs are composed of an alloy of Zn, Ag, In and S.

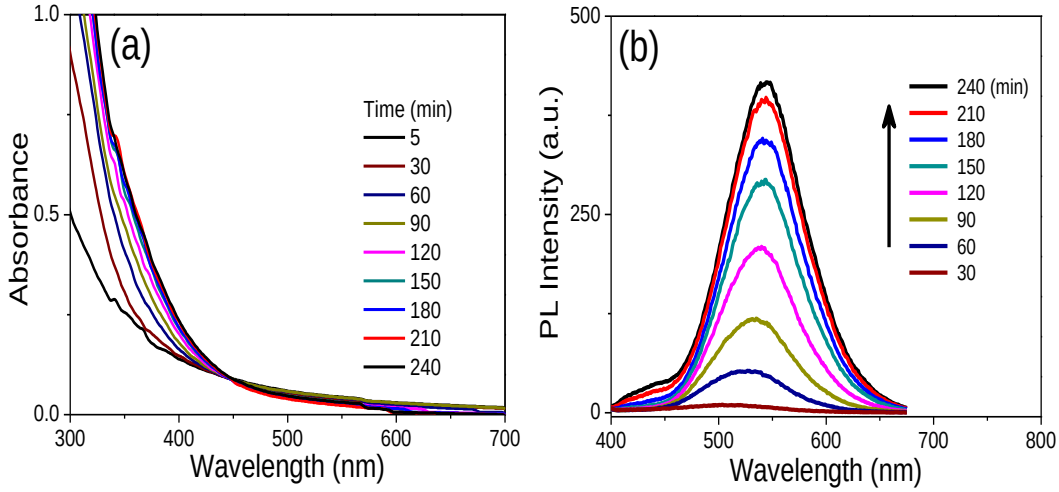

Fig. S2 Temporal evolution of the absorption (a) and PL (b) spectra of ZAIS QDs ([Zn]:[Ag]:[In]:[S(TAA)]:[GSH] = 2:0.4:2:4:16, pH8.5). As shown, in the first 30 min, only a very weak fluorescence signal can be detected; further prolonging the heating time results in the rapid increase in PL emission intensity of QDs; while the reflux time is more than 210 min, PL intensity tends to be stable. During this reflux process, PL peak position only slightly red shifted from 525 to 545 nm, which may suggest that in the present synthesis, extending the reaction time is not favorable for preparing ZAIS QDs with wide tunable PL emission.

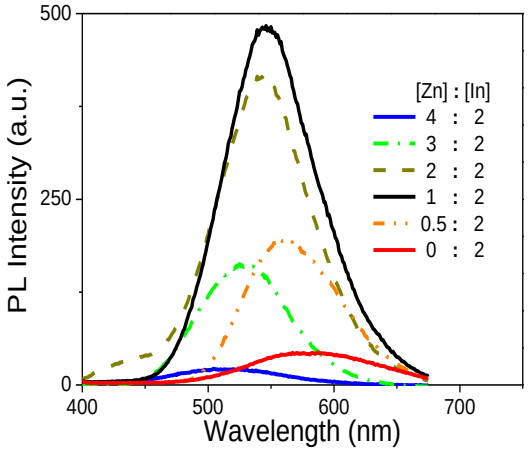

Fig. S3 PL spectra of the QD dispersions prepared with different Zn/In ratios ([Ag]:[In]:[S(TAA)]:[GSH]=0.4:2:2:4:16, pH8.5; the heating time was fixed at 240 min). In general, the presence of Zn in the reaction mixture results in a gradual blue-shift in PL peak of QDs (from 575 to 520 nm). Here, it was found that the Zn/In feed ratio plays a more important role in determining the PL intensity of QDs. With varying the feed ratio of Zn:In from 0:2 to 1:2, the PL emission intensity of QDs increases rapidly and reaches a maximum (enhancements up to 1000%). However, further increasing the Zn:In feed ratio will result in a significant decrease in the PL intensity of QDs.

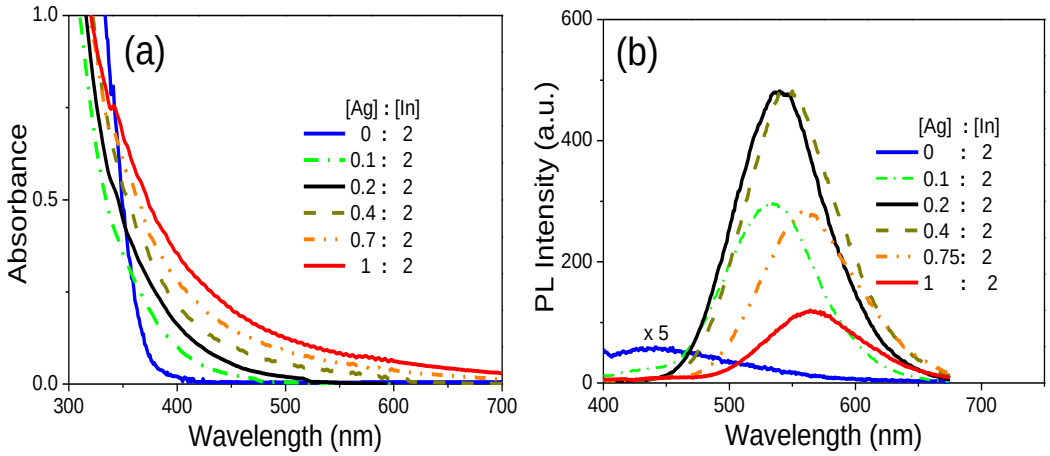

Fig. S4 Absorption (a) and PL (b) spectra of the ZAIS QDs synthesized with different Ag:In ratios ([Zn]:[In]:[S(TAA)]:[GSH]=1:2:4:16, pH8.5; the heating time was set to 240 min). As shown, the QD optical properties, especially the PL intensity, were found to be strongly dependent on the Ag:In ratio. Specifically, with increasing the ratio of Ag:In from 0:2 to 1:2, the absorption and PL spectra of the resulting ZAIS QDs are red-shifted gradually; the PL emission intensity of QDs increases and reaches a maximum at the Ag:In ratio of 0.2:2 (or 0.4:2), followed by a successive decrease.

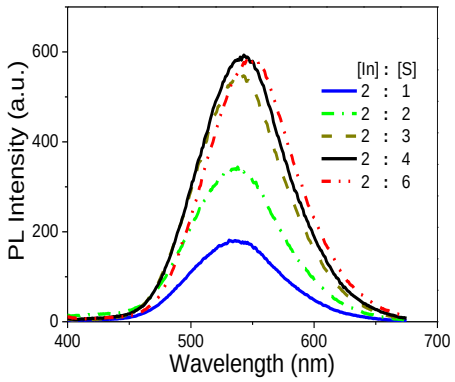

Fig. S5 PL spectra of the ZAIS QDs prepared by changing the In:S(TAA) feed ratio ([Zn]:[Ag]:[In]:[GSH]=1:0.2:2:16, pH8.5; the heating time was fixed at 240 min). With increasing the feed ratio of S:In from 1:2 to 6:2, the overall PL intensity became stronger and reached a maximum at a ratio of 2:4, whereas further increasing the amount of TAA would cause a slow decrease in PL intensity. It is worth noting that with the increase of the TAA (S source) concentration, PL peak position only slightly red shifted from 535 to 550 nm. This experimental observation is very different from previous work on ternary $AgInS_2$ QDs, where the amount of sulfur source (Na_2S) determines the PL peak position of aqueous $AgInS_2$ QDs[1].

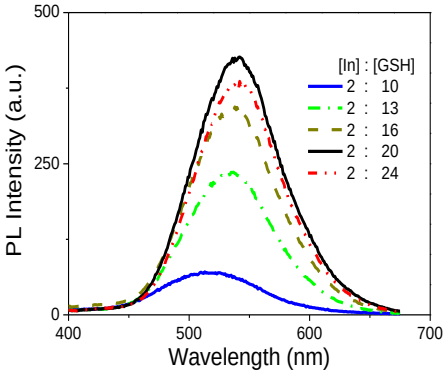

Fig. S6 PL spectra of the ZAIS QDs prepared in the presence of different concentrations of GSH ([Zn]:[Ag]:[In]:[S]=1:0.2:2:4, pH8.5; the heating time was fixed at 240 min). With increasing the GSH concentration from 10 to 24 mM, the PL emission intensity of QDs successively increases until it reaches a maximum at the GSH concentration of 20 mM. Meanwhile, we observed that the GSH concentration also affects the PL peak position of as-prepared QDs. That is, increasing the concentration of GSH results in a gradual red-shift in the emission peak from 515 to 540 nm. In addition, when the stabilizer GSH was changed to L-cysteine or *N*-acetyl-L-cysteine, the resulting dispersion does not show detectable fluorescence emission, whcih demonstrates the importance of the unique molecular structure of GSH for achieving the high PL emission of the quaternary QDs.

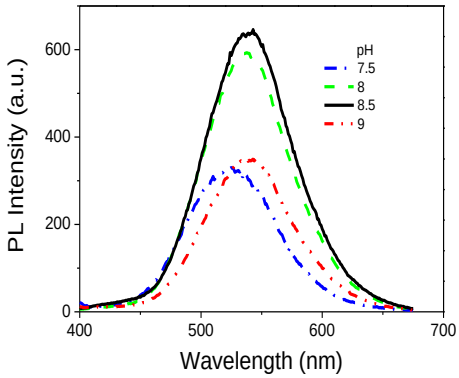

Fig. S7 PL spectra of the ZAIS QDs obtained by changing the pH value of original solution from 7.5 to 9 ([Zn]:[Ag]:[In]:[S]:[GSH]=1:0.2:2:4:20, pH8.5; the heating time was fixed at 240 min). As shown, the pH value between 8 and 8.5 is optimal for the synthesis of ZAIS QDs in water.

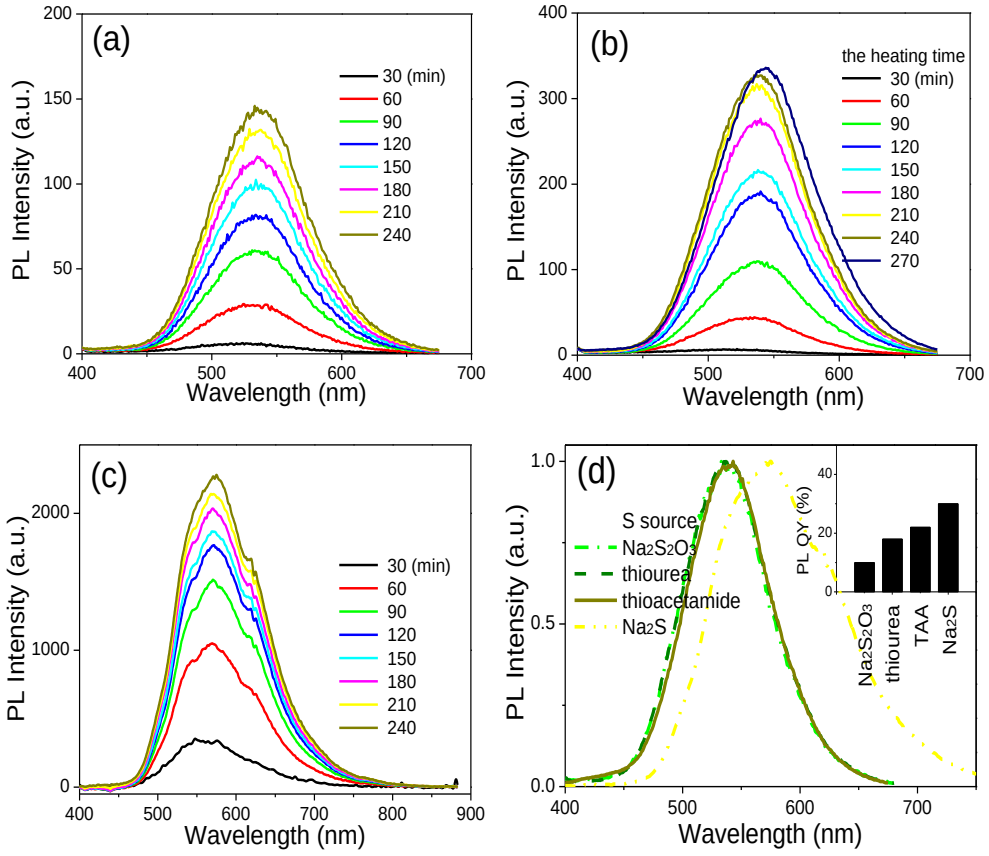

Fig. S8 Temporal evolution of PL spectra of ZAIS QDs prepared by using various aqueous S precursors: (a) $Na_2S_2O_3$, (b) thiourea, (c) Na_2S ([Zn]:[Ag]:[In]:[S]:[GSH] = 1:0.2:2:4:20, pH8.5). In this study, four kinds of various S sources (i.e., TAA, $Na_2S_2O_3$, thiourea and Na_2S) that have different reactivities were used as S sources. As compared with moderately reactive TAA, thiourea and $Na_2S_2O_3$ are poorly reactive. When the system is heated at 100 °C, thiourea or $Na_2S_2O_3$ hydrolyzes slowly to release free S^{2-} ions, which reacts with cations to

produce ZAIS QDs. However, Na_2S is highly reactive, which can react with cations directly, even at room temperature (without heating). As shown, the reactivity of the aqueous S precursor plays an important role in determining the PL properties of the resulting aqueous ZAIS QDs. For instance, when using lowly reactive S precursors (e.g., TAA, thiourea and $Na_2S_2O_3$) as S sources, the as-prepared ZAIS QDs exhibit similar PL emission wavelengths (~545 nm; PL bandwidth, ~80 nm), and the QDs prepared from moderately reactive TAA is found to have the most favorable PL emission (PL QY, 22%); however, with using highly reactive Na_2S, under the same conditions, the as-prepared ZAIS QDs show long-wavelength PL emission (PL peak, ~575 nm) with higher PL QY (30%) and wider bandwidth (~130 nm).

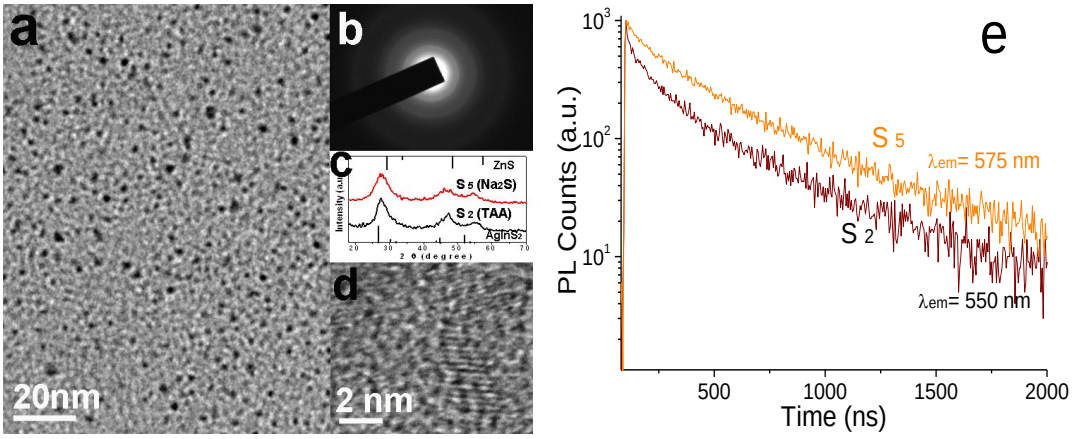

Fig. S9 TEM (a) and HRTEM (d) images and SAED pattern (b) of the sample S_2. (c) The XRD patterns of the samples S_2 and S_5 (the line patterns of cubic ZnS and tetragonal $AgInS_2$ are provided for comparison). Due to the small size of these samples, the XRD peaks were broad and weak for both samples. All diffraction peaks between those of bulk tetragonal $AgInS_2$ and cubic ZnS indicate the formation of quaternary ZAIS QDs. In addition, as compare to Na_2S, using TAA (thiourea or $Na_2S_2O_3$) as an S source was observed to result in a slight decrease in the diameter of ZAIS QDs. (e) Time-resolved PL lifetime spectra of the typical samples S_2 and S_5 recorded at the corresponding maximum emission wavelength (λ_{ex}=405nm). The fluorescence lifetime of S_5 is longer than that of S_2 since the sample S_5 has higher PL QY (Table 1).

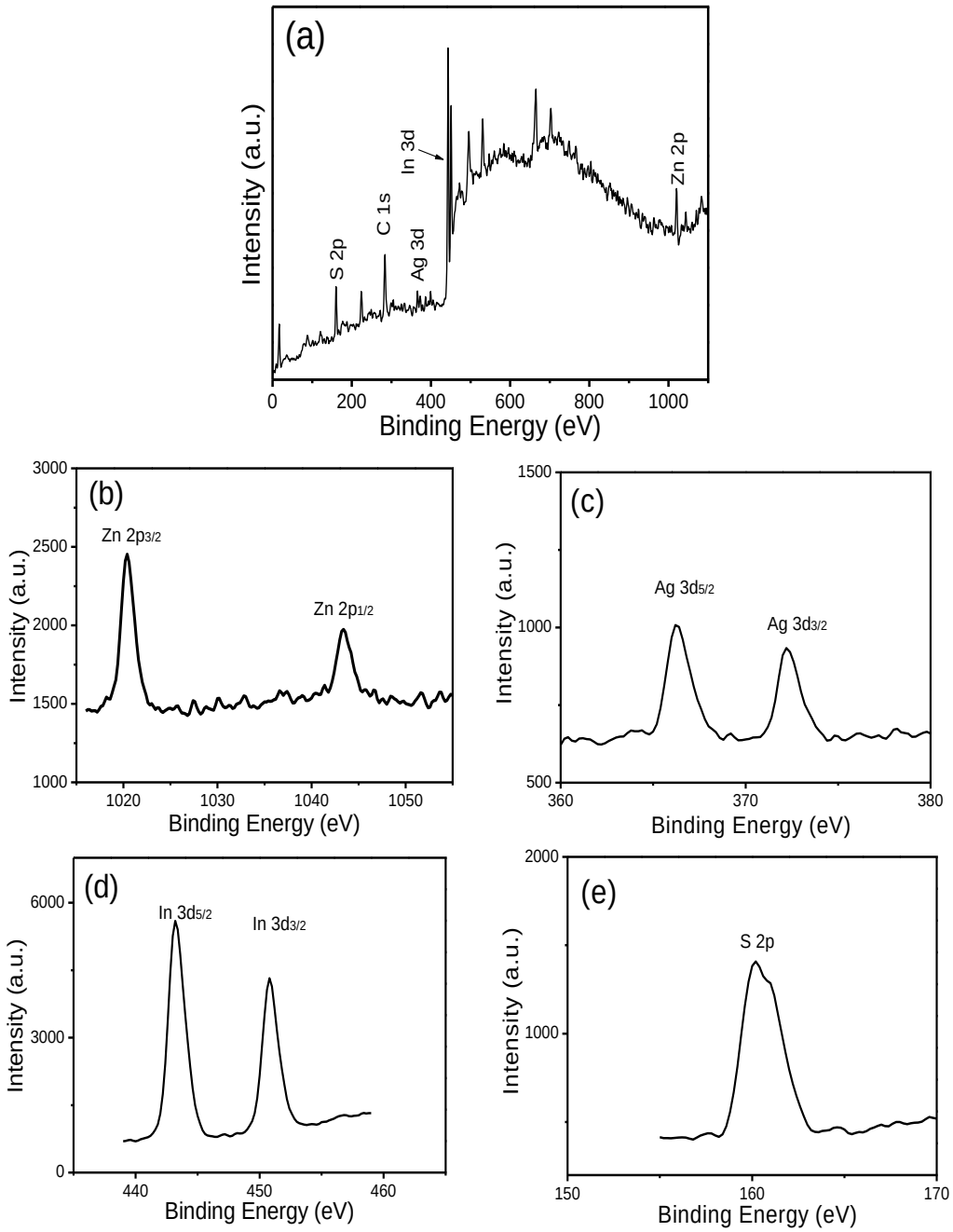

Fig. S10 (a) The survey spectrum of the sample S_2. The corresponding XPS spectra of Zn 2p (b), Ag 3d (c), In 3d (d) and S 2p (e) of the sample S_2 (the Zn/Ag/In/S feed ratio is 1:0.2:2:4; the heating time is 210 min).

Table S1 The size and chemical composition of the ZAIS QDs obtained by TEM and XPS measurements

Sample	PL Peak (nm)	Size (nm)	Zn/(Zn+Ag+In)	Zn	Ag	In
S_2	545	2	25.8%	0.198	0.054	0.516
S_4	560	2.5	26.8%	0.209	0.069	0.504
S_5	575	2.5	23.3%	0.181	0.075	0.521
S_7	625	2	6.9%	0.071	0.500	0.451

Table S2 PL properties of water-soluble citrate-stabilized CdSe/CdS QDs,[2,3] *N*-acetyl-L-cysteine-stabilized CdTe QDs[4,5] and GSH-stabilized ZAIS QDs

properties	CdSe/CdS QDs	CdTe QDs	ZAIS QDs
Spectral tunable range	530–610	500–800 nm	525–625 nm
PL QY	>20%	>30%	15–30%
fwhm	40	>40	>80 nm

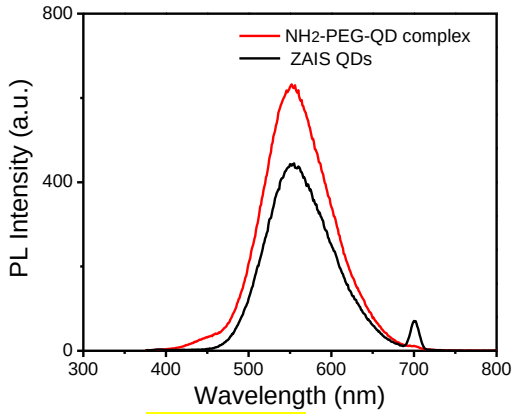

Fig. S11 Photoluminescence spectra (λ_{ex}=350 nm) of the initial aqueous ZAIS QDs and the NH_2-PEG_{2000}-QD complex.

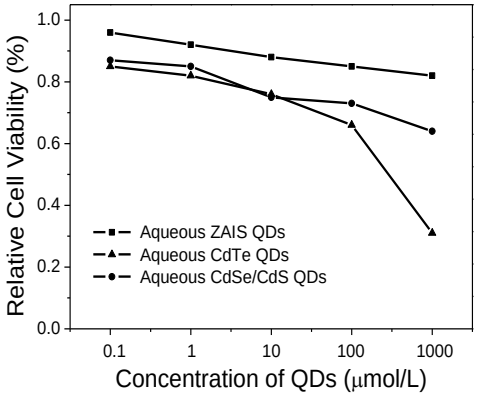

Fig. S12 *In vitro* cytotoxicity of the aqueous GSH-capped ZAIS QDs, the citrate-capped CdSe/CdS QDs, and *N*-acetyl-L-cysteine-capped CdTe QDs determined by MTT (3-(4,5-dimethylthialzol-2-yl)-2,5-diphenyltetrazolium bromide) assay. Human umbilical vein endothelial (HUVEC) cells were cultured with medium containing different concentrations of aqueous QDs for 48 h. The three kinds of QDs studied have similar PL maximum (~560 nm).

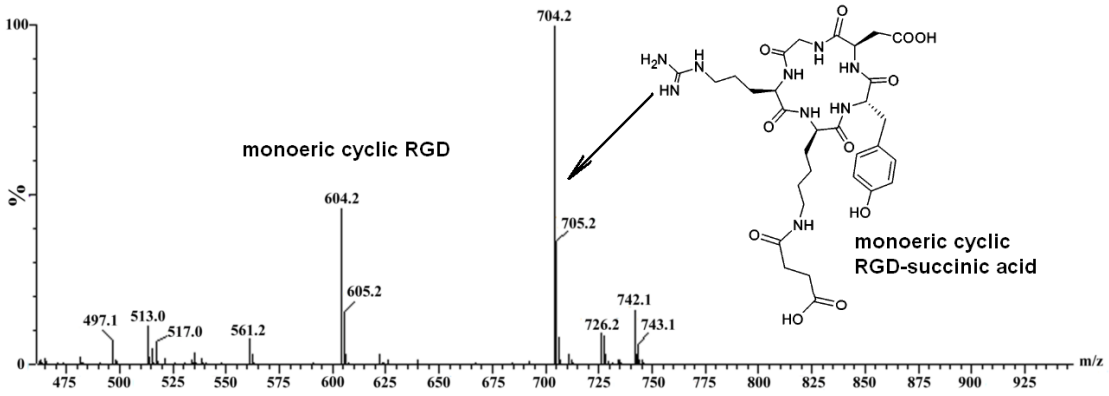

Fig. S13 The mass spectrum of monoeric cyclic RGD-succinic acid prepared from the reaction between monoeric cyclic RGD and succinic anhydride. Inset, the structure of monoeric cyclic RGD-succinic acid.

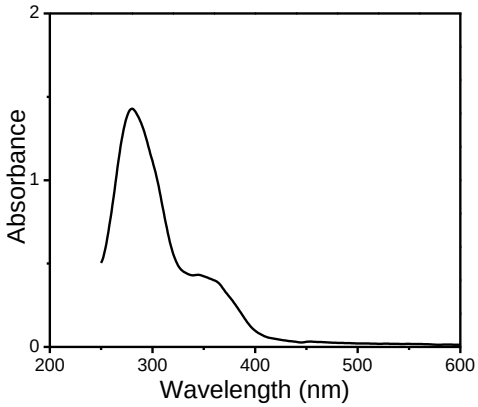

Fig. S14 The absorption spectrum of folic acid in water containing DMSO.

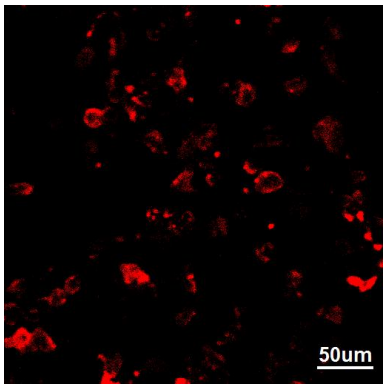

Fig. S15 The fluorescent image of the A549 cells labeled with yellow-emitting ZAIS QDs under 488 nm excitation (inset: cell imaging with higher magnification). Here, the incubation time is set to two hour, and the concentration of QDs used is 0.1 mM (the value refers to the S content of the QDs). The orange emission was clearly observed from the cells, fluorescence appeared in the cytoplasm region rather than in the nucleus. This result indicated that the initial ZAIS QDs did not translocate into the cell nucleus.

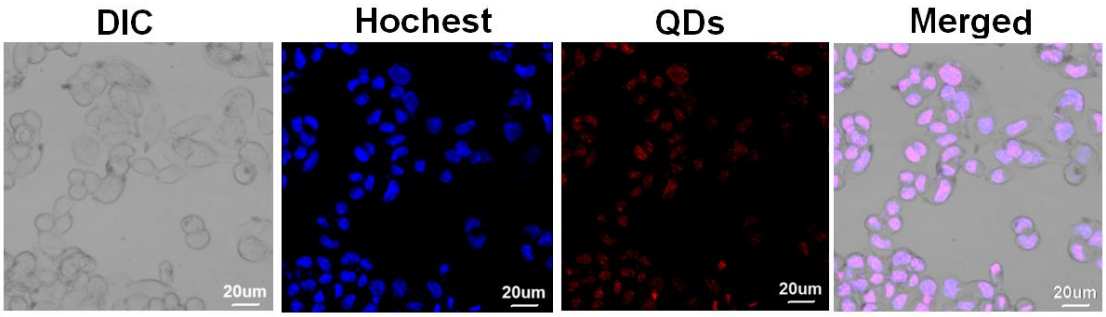

Fig. S16 The LCSM images of Bel-7402 cells incubated with 0.1 mM of CH_3O-PEG_{2000}-capped ZAIS QDs at 37 °C for 1 h. The cells were counterstained with Hochest (blue) for the cell nucleus.

References

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