Supplementary Information

Synthesis of Far-Red- and Near-Infrared-emitting Cu-doped InP/ZnS (Core/Shell) Quantum Dots with Controlled Doping Step and their Surface Functionalization for Bioconjugation

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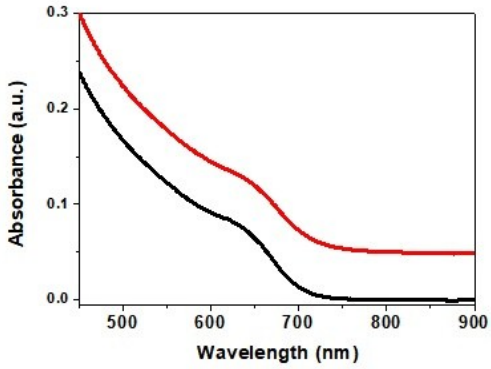

Figure S1. Absorption spectra of undoped InP/ZnS QDs(black) and Cu:InP/ZnS d-dots(red) quantum dots (QD) for samples shown in Figure 1.

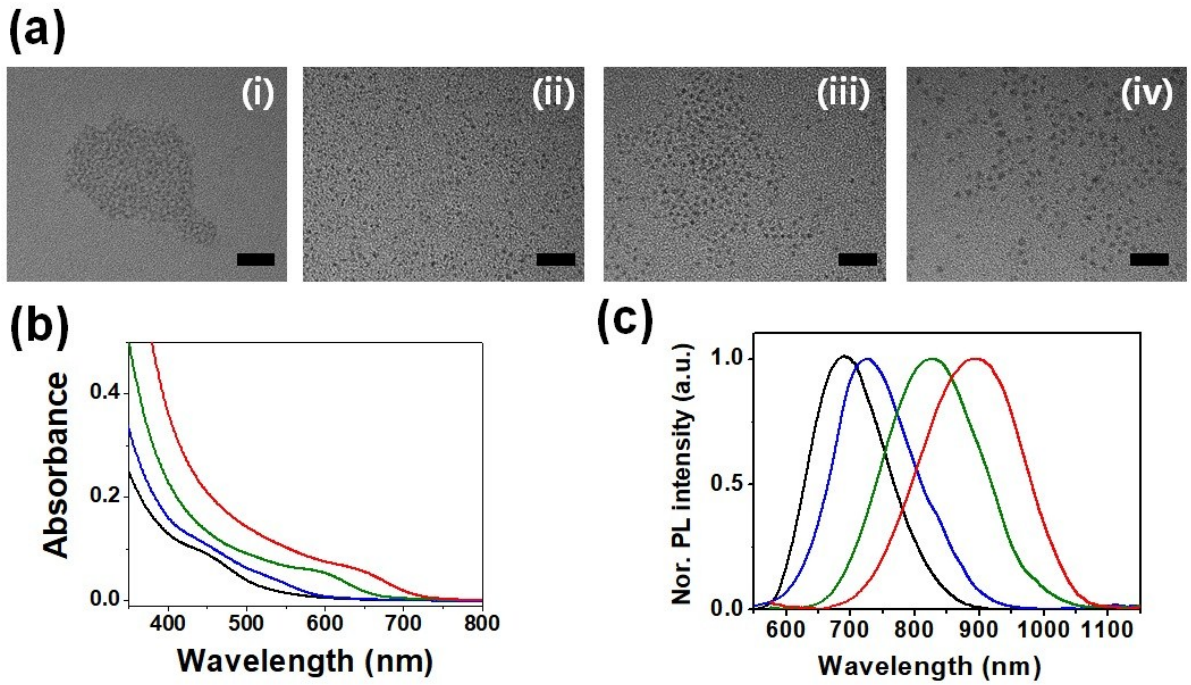

Figure S2. (a) Transmission electron microscope (TEM) images of differently sized Cu doped InP quantum dots (QD) samples (scale bar: 20 nm), where: (i) black-sample, (ii) blue-sample, (iii) green-sample, and (iv) red-sample. Average particle sizes are 1.83 nm (i), 2.16 nm (ii), 2.92 nm (iii), 3.39 nm (iv), respectively. (b) Absorption and (c) photoluminescence (PL) spectra of the corresponding Cu doped InP QD samples.

** InP QD samples of sizes 2.92 nm and 3.39 nm were prepared by repeated alternating injections of additional indium and phosphorus precursors in the InP QD growth solution[R1] at 210 °C until the desired size was achieved.*

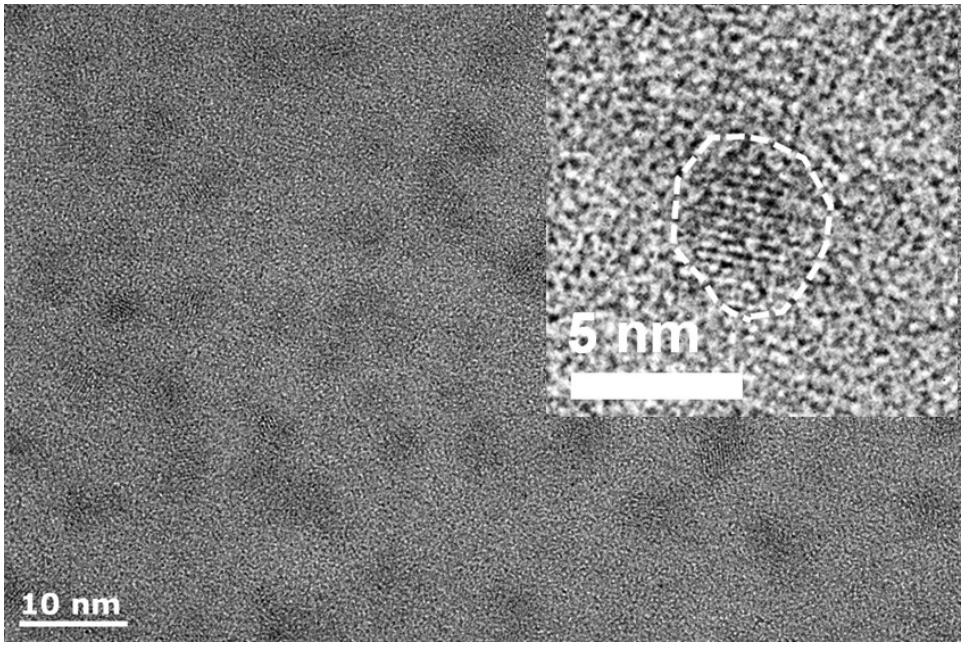

Figure S3. HR-TEM image of InP/ZnS:Cu/ZnS (3MLs) QDs. The partially magnified image is shown in the inset panel)

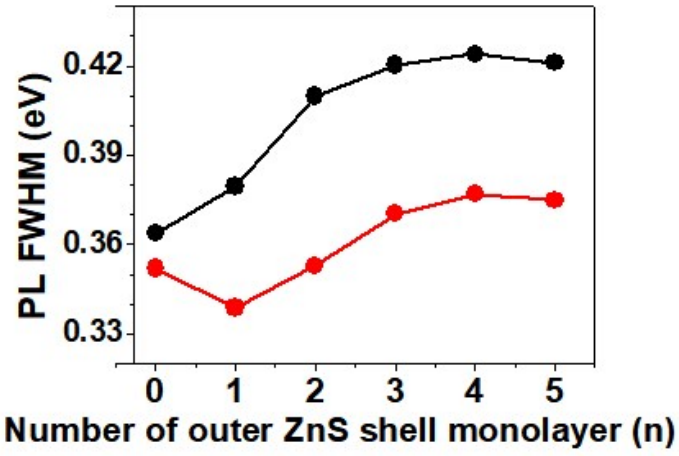

Figure S4. Photoluminescence full-width at half-maximum (FWHM) values as functions of outer shell thickness for the InP:Cu/ZnS QD (black) and InP/ZnS:Cu/ZnS QD (red) samples shown in Figure 2.

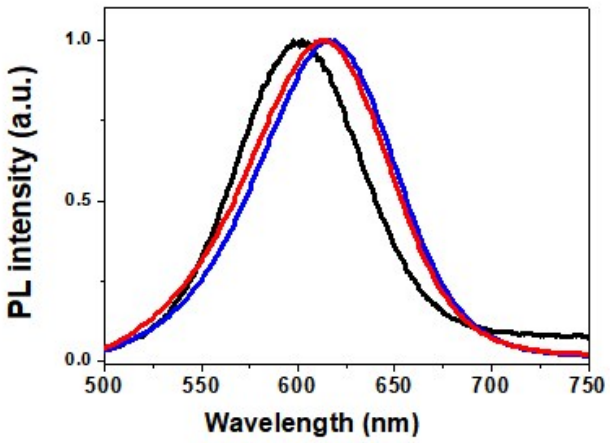

Figure S5. Photoluminescence spectra of bare InP quantum dots (QDs; black), InP/ZnS (core/shell) QDs with 2 ML of ZnS shell (red), and 4 ML of ZnS shell (blue).

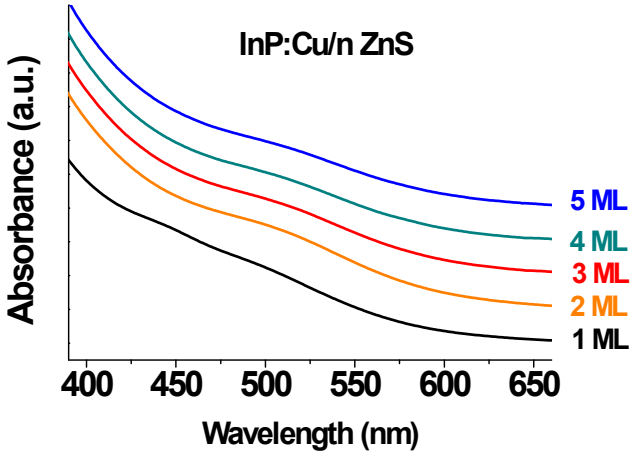

Figure S6. Absorption spectra of the InP:Cu/ZnS QDs with varying the ZnS shell thickness that represented in Figure 2.

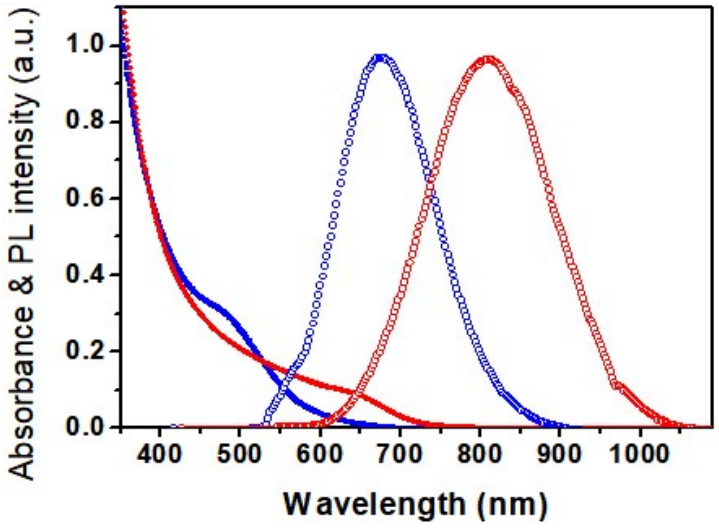

Figure S7. Absorbance (filled circle) and photoluminescence (open circle) spectra of the far-red (blue) and NIR (red) emitting InP/ZnS:Cu/ZnS QD samples dispersed in hexanes.

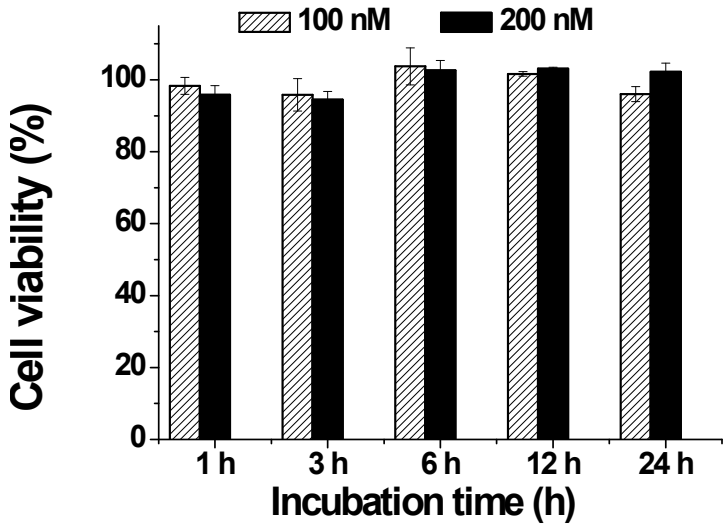

Figure S8. Cytotoxicity assays of InP/ZnS:Cu/ZnS quantum dots (QDs) in MDA-MB-231 cells by cell counting kit-8 assay. Cells were incubated with 100 nM or 200 nM QD probes for 1-24 h at 37ºC. Measurement results are expressed as the ratio between the absorbance of the sample and that of negative control cells that had not experienced sample incubation.

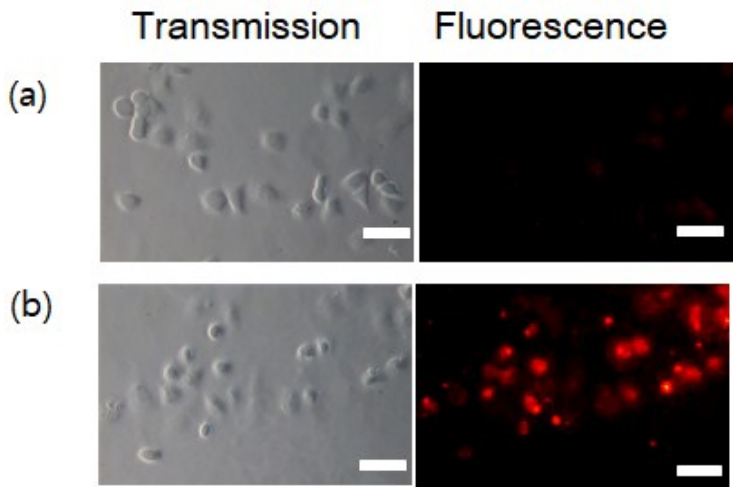

Figure S9. Transmission (left) and fluorescence (right) optical-microscope images of HER2-positive SK-BR-3 cells treated with 676-nm-emitting (a) DHLA/ZW-InP/ZnS:Cu/ZnS QDs and (b) DHLA/ZW-InP/ZnS:Cu/ZnS QDs conjugated with anti-HER2-antiibody (Scale bar: 50 μm).

Table S1. Room-temperature tri-exponentail photoluminescence decay fit parameters of the undoped and Cu doped quantum dot (QD) samples shown in Figure 1d, Figure 2d, and Figure 2e.

(1) Samples represented in Figure 1d

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	τ_{ave} (ns)
InP/ZnS QDs	15.9	1	69.8	31	14.3	78	47
InP/ZnS:Cu QDs	51.8	2	7.9	47	40.3	570	559

(2) Samples represented in Figure 2d

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	τ_{ave} (ns)
InP:Cu QDs	63.9	2	24.2	33	12.0	213	164
InP:Cu/ZnS QDs	26.4	1	34.3	73	39.2	364	320

(3) Samples represented in Figure 2e

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	τ_{ave} (ns)
InP/ZnS:Cu QDs	30.7	1	32.4	43	36.9	322	292
InP/ZnS:Cu/ZnS QDs	22.1	1	21.4	78	56.5	357	335

PL decay time constants (τ_i), and corresponding amplitude percentages (A). τ_{ave} is intensity-weighted average lifetime.

[Reference]

R1. D. Battaglia and X. Peng, *Nano Lett.*, 2002, **2**, 1027-1030.