

Electronic Supplementary Information (ESI)

Glucose/Galactose/Dextran-Functionalized Quantum Dot, Iron Oxide and Doped Semiconductor Nanoparticle with < 100 nm Hydrodynamic Diameter

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Preparation of silica coated QD: Silica coated QD was prepared using our earlier method.³⁷ In brief, 4.0 mL of purified QD solution in toluene (absorbance ~ 1.0 at longest wavelength) was taken in a 15 ml glass. Then 4 μ L of MPS and 20 μ L of AEAPS were added under stirring condition. After that, the solution was heated at 60-80 $^{\circ}$ C. QD began precipitating after 3-4 minutes and heating was continued for 10-15 mins. Then, the precipitate was washed once with toluene and twice with ethanol. Finally, precipitated particles were dispersed in 2 mL of distilled water.

Biochemical activity test using galactose/glucose/dextran functionalized QD: Two sets of PL cuvette each containing 2 mL of negatively charged galactose functionalized QD solution were taken in phosphate buffer of pH 7.4. Then 20 μ L (12 mg/mL) RCA₁₂₀ was added to one cuvette and 200 μ L of 100 μ M BSA to another cuvette as control experiment. In another control experiment, 2 mL of negatively charged polymer-coated QD without any galactose functionalization was taken in PL cuvette and mixed with 20 μ L (12 mg/mL) RCA₁₂₀. Selective binding between RCA₁₂₀ and galactose functionalized QD leads to particle aggregation, (Figure 2.a,ii) which was observed in few minutes after

mixing RCA₁₂₀. But no such precipitation was observed when RCA₁₂₀ was added to the QD solution without any galactose functionalization or BSA added to QD-galactose solution (Figure S9a).

Similarly, we did the carbohydrate-glycoprotein binding study between glucose/dextran functionalized QD and Con-A. Two sets of PL cuvette each contains 2 mL of dextran/glucose functionalized QD solution was taken in a PL cuvette containing phosphate buffer of pH 7.4. Next, 200 μ L of 100 μ M of Con-A was added to one of the cuvette whereas 200 μ L of 100 μ L of BSA was added to another cuvette as control experiment. In additional control experiments, QD without any dextran/glucose functionalization was mixed with Con-A solution. Selective binding between Con A and glucose/dextran functionalized QD leads to particle aggregation, (Figure 2a,i) which was observed in few minutes after mixing Con A. But no precipitation was observed when Con A was added to the QD solution without glucose/dextran functionalization or BSA was added to the glucose/dextran functionalized QD solution (Figure S9b). This type carbohydrate-glycoprotein binding study was also performed for Mn-ZnS-glucose and (Figure 2a,iii), γ -Fe₂O₃-fluorescein-glucose (Figure 2a,iv) and silica coated QD-glucose (Figure S3,b) and similar results were observed.

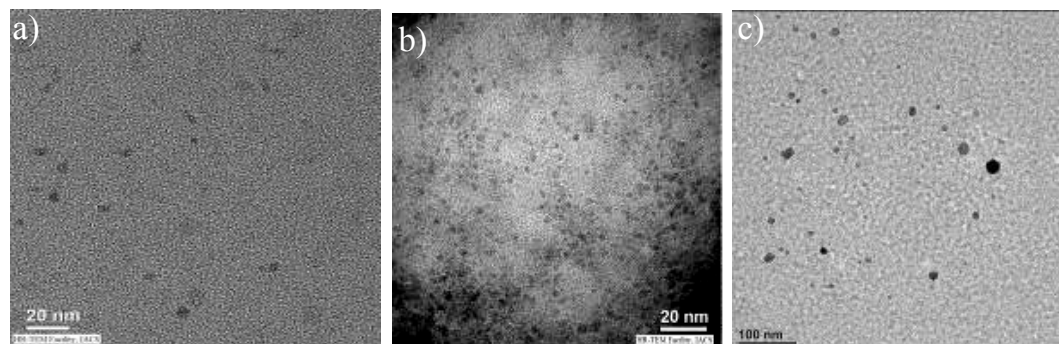


Figure S1. TEM image of carbohydrate functionalized QD (a), Mn doped ZnS (b) and γ -Fe₂O₃-fluorescein (c).

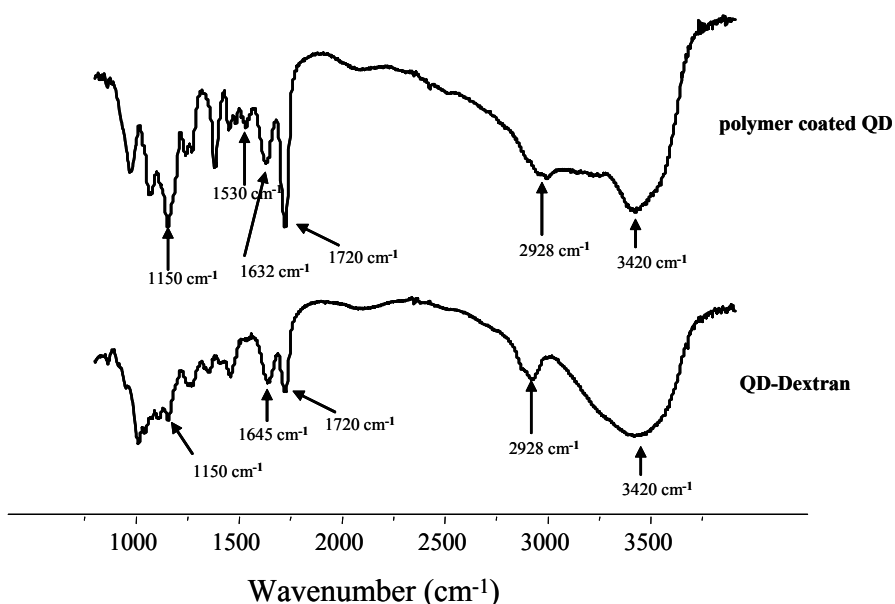


Figure S2: FTIR spectra of QD and dextran functionalized QD. It shows that rocking (1150 cm⁻¹) and symmetry deformed vibration (1530 cm⁻¹) of $-\text{NH}_3^+$ becomes absent or gets weakened after carbohydrate functionalization. In addition 1632 cm⁻¹ peak due to N-H bending vibration of primary amine gets weaken and shifts to 1645 cm⁻¹ after carbohydrate functionalization. This result suggests that $-\text{NH}_2$ groups are reacted with carbohydrates. Signature of carbohydrate is also confirmed from the increase of C-H stretching intensity at 2928 cm⁻¹ and broadening of stretching vibration of O-H at 3420 cm⁻¹.

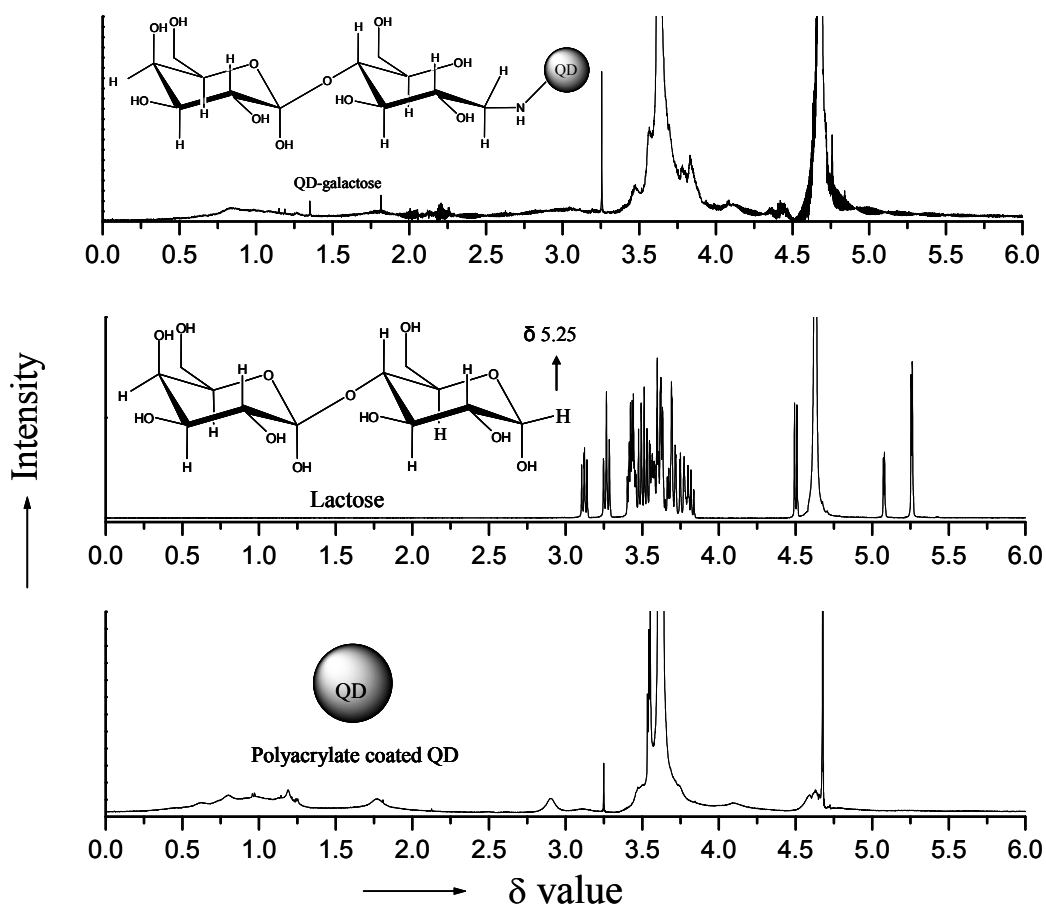


Figure S3: NMR data of lactose (middle panel) and polyacrylate coated QD before (lower panel) and after galactose functionalization.(upper panel) Result shows the signature of protons associated with carbohydrate moiety with δ value between 3.25 to 4 present in QD-galactose and absence of any peak for δ value of 5.3 and 5.1 due to protons at reducing end. This result indicates the successful conjugation and absence of any free carbohydrate in the purified QD-galactose.

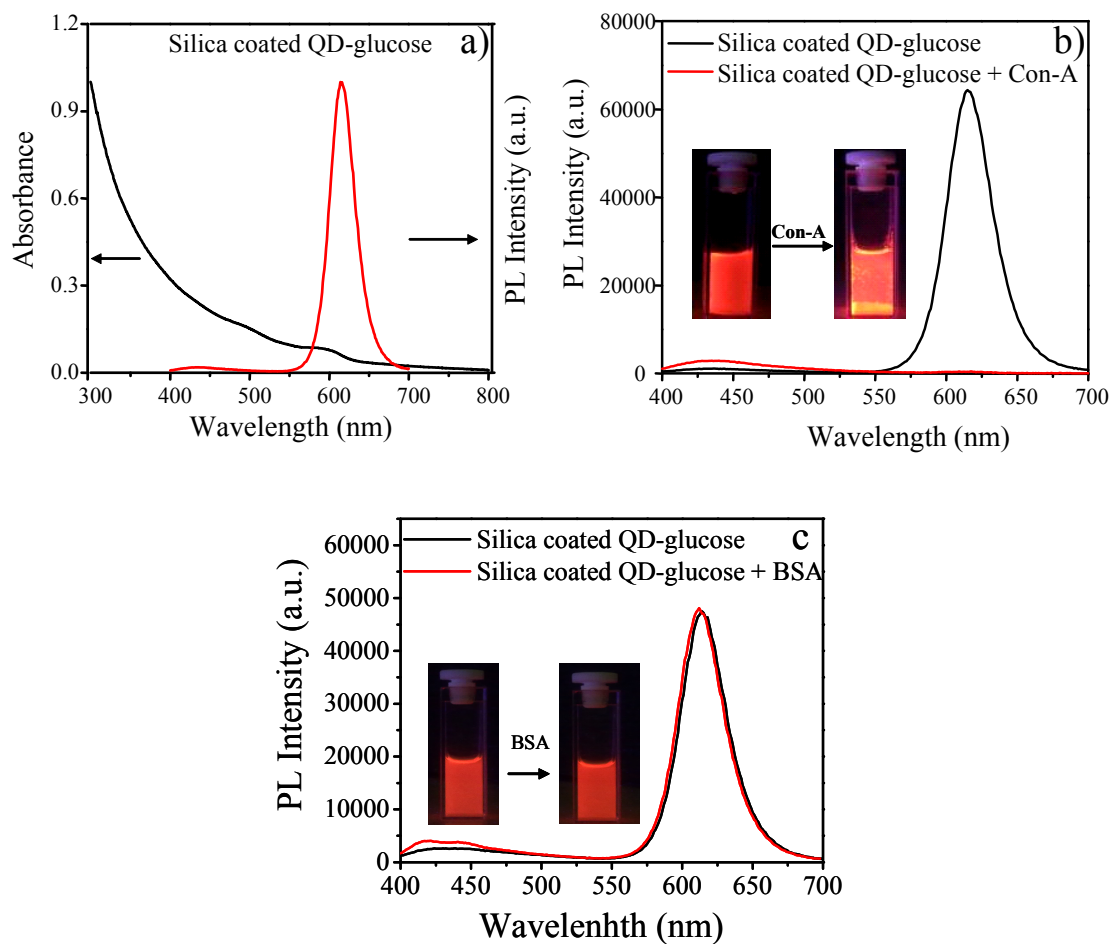


Figure S4: Glucose functionalized QD prepared from silica coated QD. Absorption and emission spectra of silica coated red emitting QD which is functionalized with glucose (a) and their Con A induced precipitation (b) and control experiment with BSA showing no QD precipitation (c). After adding Con A, floated QDs aggregates were removed by centrifuge, prior to obtain fluorescence spectra of supernatant.

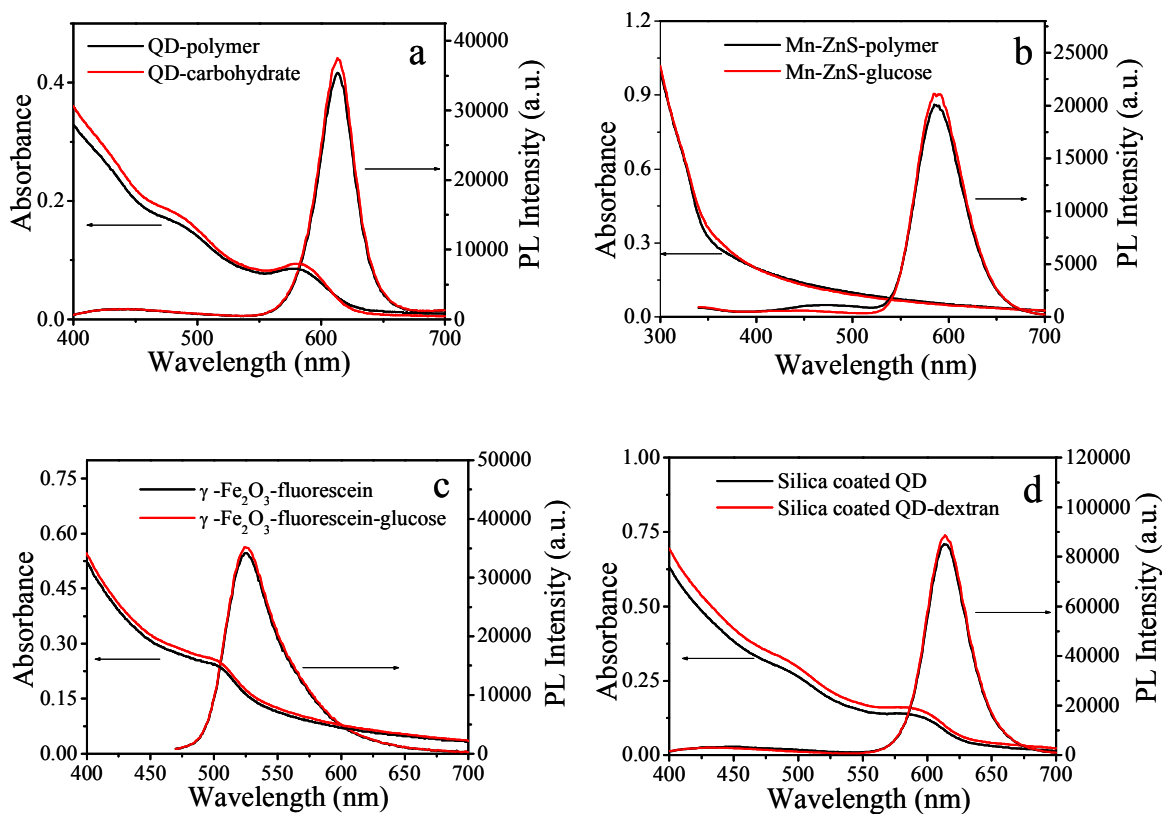


Figure S5: UV-visible and PL spectra of polymer coated nanoparticles (black line) and after functionalization with carbohydrate (red line). a) QD, b) Mn doped ZnS, c) γ -Fe₂O₃-fluorescein and d) silica coated QD.

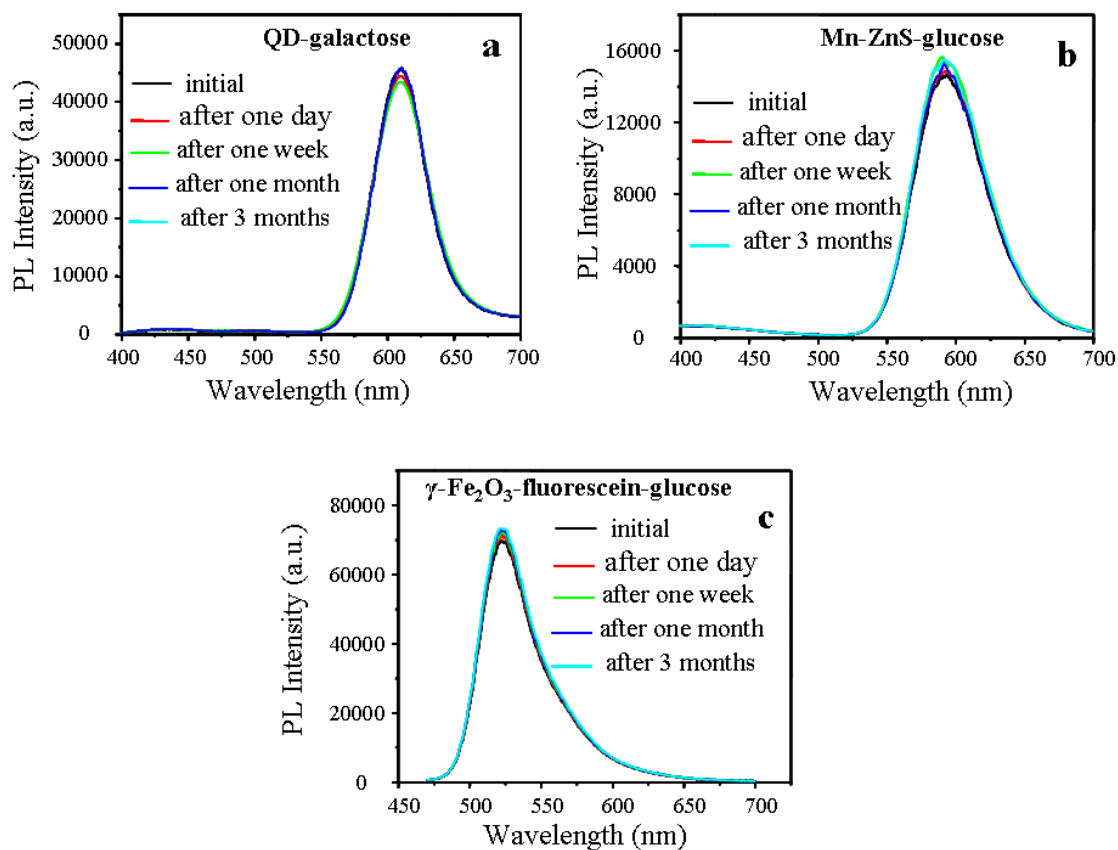


Figure S6: Stability of carbohydrate functionalized nanoparticles after preserving for different time. (a) QD-galactose ($\lambda_{\text{ex}} = 370$ nm), (b) Mn-ZnS-glucose ($\lambda_{\text{ex}} = 320$ nm) and (c) γ -Fe₂O₃-fluorescein-glucose ($\lambda_{\text{ex}} = 450$ nm).

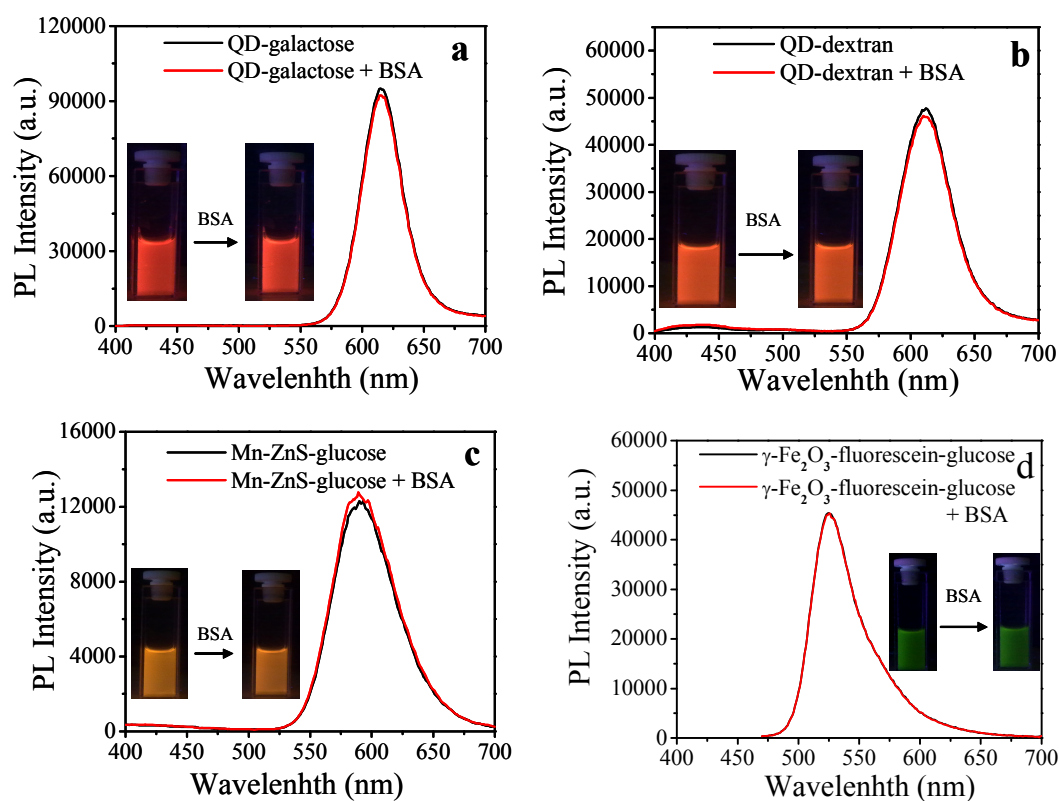


Figure S7: Control precipitation experiment of carbohydrate functionalized nanoparticle with bovine serum albumin (BSA) protein. As BSA has no specific interaction with glucose, dextran and galactose, therefore it has no effect on glucose/dextran/galactose functionalized nanoparticles which were indicated by unaltered PL spectra and digital images. a) QD-galactose, b) QD-dextran, c) Mn-ZnS-glucose and d) γ -Fe₂O₃-fluorescein-glucose.

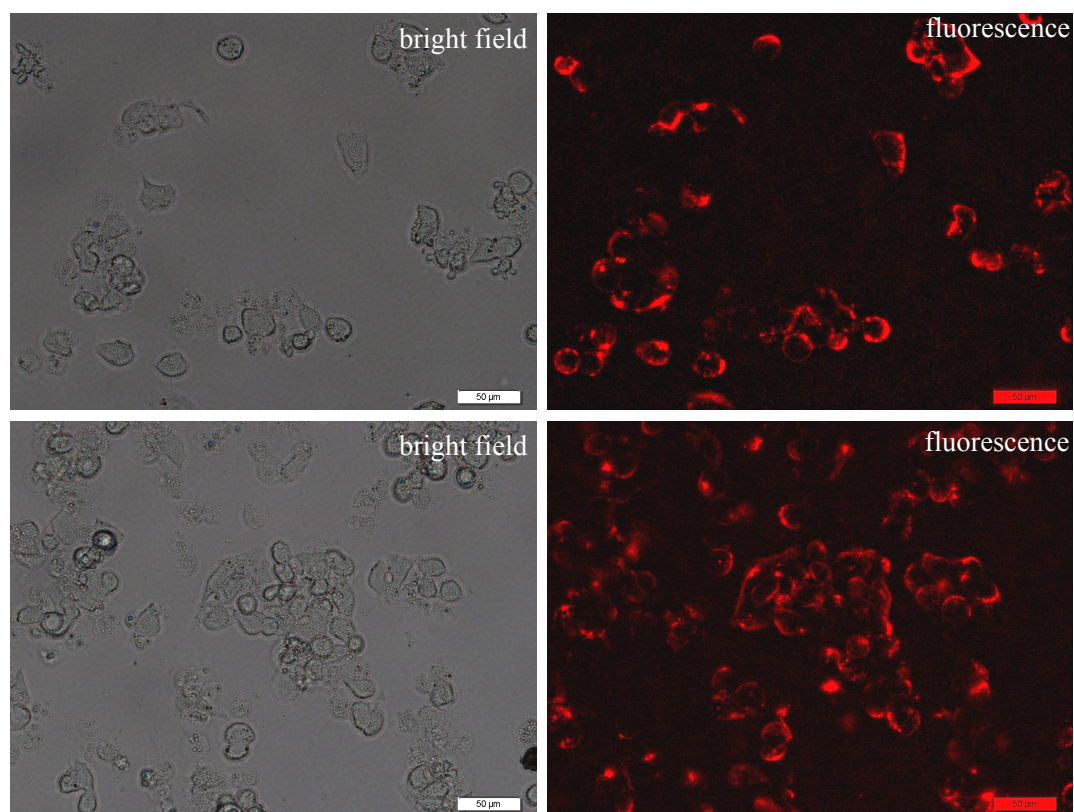


Figure S8. Bright field and fluorescence image of HepG2 cells labeled with galactose functionalized QD using different batches of QD-galactose, showing highly reproducible selective labeling of HepG2 cells by QD-galactose.

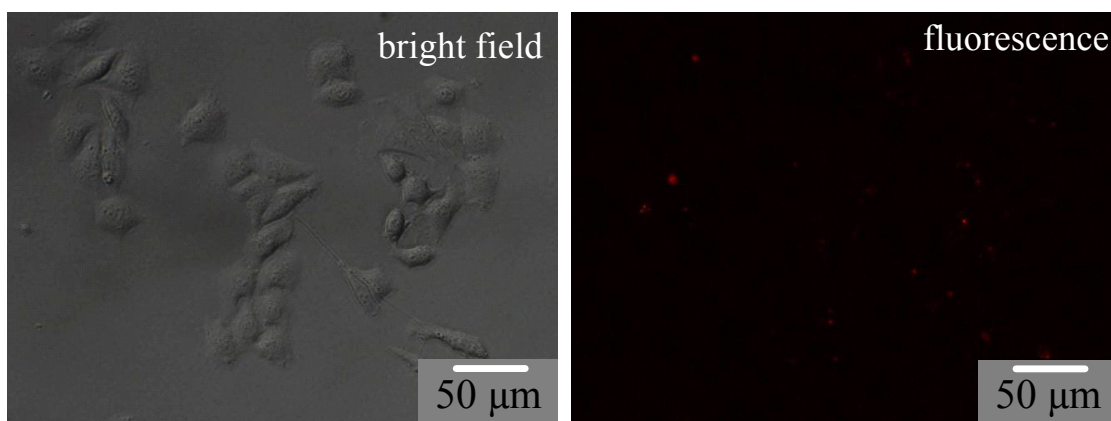


Figure S9: Control cell labeling experiment of galactose functionalized QD using HeLa cells. This control experiment indicates that galactose functionalized QD do not label HeLa cells due to absence of galactose receptors.

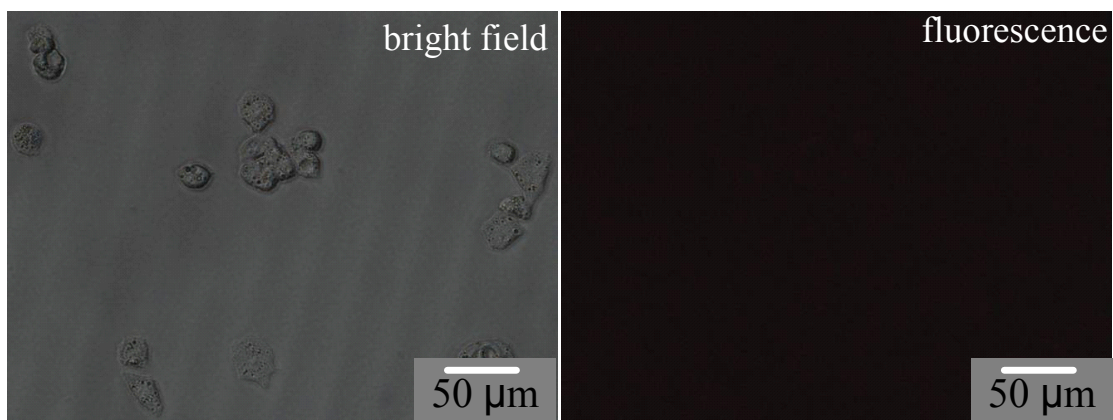


Figure S10: Control experiment of cellular uptake study of glucose functionalized QD to HepG2 cells. Result proves that glucose functionalized QD do not interact and do not label HepG2 cells.

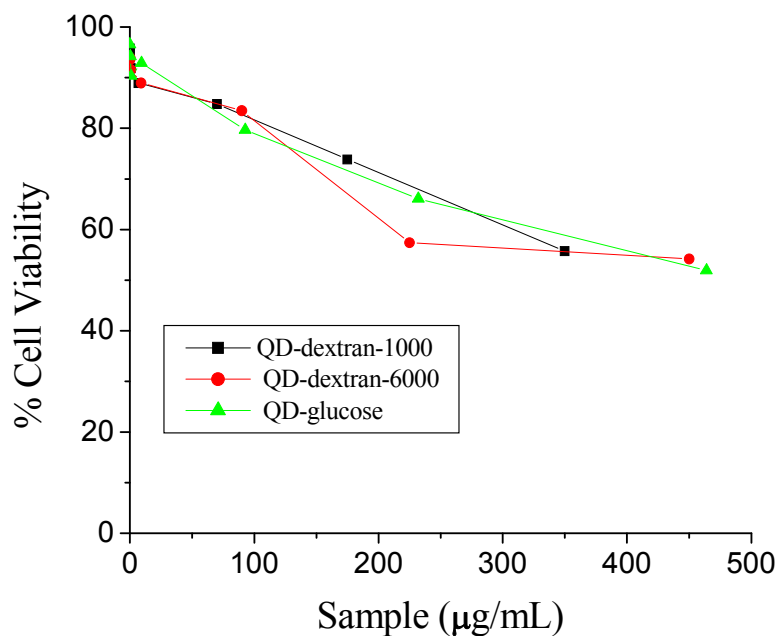


Figure S11: Viability test of HeLa cells using carbohydrate functionalized QD, showing that cell have good viability at lower dose of functional QD.

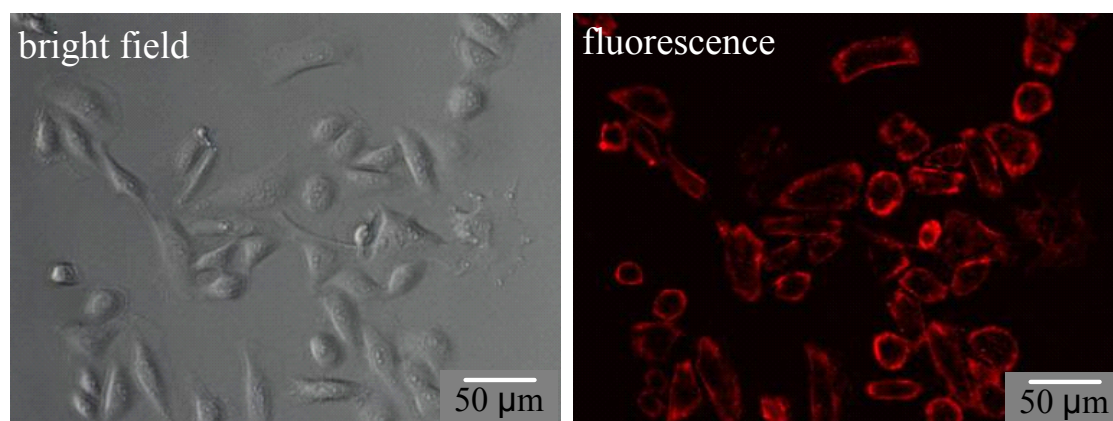


Figure S12: Cellular uptake of polymer coated QD by HeLa cells. Surface of this type of QD was modified in such a way that it contains both positive charges (due to primary amine groups) and negative charges (due to sulfopropyl groups), leading to nonspecific binding to the HeLa cells.