

## Supplementary Information

A facile method to prepare high-performance magnetic and fluorescent bifunctional nanocomposites and their preliminary application in biomolecule detection

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### Synthesis of SiO<sub>2</sub> co-encapsulating Fe<sub>3</sub>O<sub>4</sub> and QDs<sup>1,2</sup>

Typically, 10 mL of cyclohexane, 1.3 mL of NP-40, 200 μL of Fe<sub>3</sub>O<sub>4</sub> (3 nmol), 100 μL of QDs (3 nmol), and 50 μL of TEOS were in turn added into a flask under vigorous stirring. 30 minutes later, 30 μL of ammonia aqueous solution (25 wt%) was introduced to the flask. The silica growth was completed after 24 h of stirring at RT. Then, 10 μL of APTES was loaded to the system to introduce amine groups onto the surface of the nanoparticles for 24 h. The resulting nanoparticles were isolated from the microemulsion using ethanol to remove surfactant and unreacted molecules. A magnet was put on the side of the centrifuge tube to attract the MNQDs nanocomposite to the side, and then the solution was removed and 2 mL of deionized water was added to redisperse the nanocomposites by ultrasonics. The magnetic separation process was repeated twice. Finally, the nanocomposites were dispersed in 2 mL of deionized water, and the solution was extracted and passed through a 0.22 μm filter.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-CdZnSeS@PSMA

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub><sup>1</sup>

Typically, 10 mL of cyclohexane, 1.3 mL of NP-40, 200 μL of Fe<sub>3</sub>O<sub>4</sub> (3 nmol), and 50 μL of TEOS were in turn added into a flask under vigorous stirring. 30 minutes later, 30 μL of ammonia aqueous solution (25 wt%) was introduced to the flask. The silica growth was completed after 24 h of stirring at RT. Then, 10 μL of APTES was loaded to the system to introduce amine groups onto the surface of the nanoparticles for 24 h. The resulting nanoparticles were isolated from the microemulsion using ethanol to remove the surfactant and unreacted molecules. A magnet was put on the side of the centrifuge tube to attract the Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> nanocomposite to the side, and then the solution was removed and 5 mL of deionized water was added to redisperse the nanocomposites by ultrasonics. The magnetic separation process was repeated twice. Finally, the nanocomposites were dispersed in 0.5 mL of deionized water.

#### Synthesis of CdZnSeS@PSMA<sup>2</sup>

100 μL of QDs (3 nmol) were added to 1 mL CHCl<sub>3</sub> with 30 nmol PSMA. The reaction mixture was stirred at room temperature for 3 h. Then, 150 nmol of JMP was introduced into the system, 12 h later, 5 mL of NaOH (0.01 mol/mL) solution was added and stirred for 30 min at RT. The sample was centrifuged at 7000 rpm for 5 min to speed up the separation of the CHCl<sub>3</sub> and water phases. Then, the particles were separated by centrifuge at 20000 rpm for 30 min and washed two times. Finally, the sample was dispersed

in 0.5 mL of deionized water.

#### Conjugation of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> and CdZnSeS@PSMA

0.5 mL of the prepared Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> solution and 0.5 mL of the prepared CdZnSeS@PSMA solution, were added to 2 mL of phosphate buffered saline (PBS) buffer containing 0.5 mg of EDC·HCl with gentle shaking for 2 h at RT. Then, a magnet was put on the side of the centrifuge tube to attract the Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-CdZnSeS@PSMA to the side, and the enriched particles were resuspended in 5 mL deionized water, the enrichments and separation of nanocomposites by the magnet were repeated twice to get rid of the free CdZnSeS@PSMA particles. Finally, the nanocomposites were dispersed in 2 mL of deionized water.

#### Cytotoxicity assay

The cell viability was *in vitro* measured by using 3-(4,5-dimethylthiazol-2-yl)-2,5 diphenyl-tetrazolium bromide (MTT) proliferation assay. HeLa Cells were seeded into a 96-well micro-plate with 5000 cells/well and then pre-incubated at 37 °C for 24 h under 5% CO<sub>2</sub>. Following that, DMEM solutions containing MNQDNCs/JMP (or MNQDNCs/EA) with different concentrations of 19, 38, 75, 150, 300, and 600 µg/mL were added to the wells. Subsequently, the cells were incubated for another 24 h in the incubator at 37 °C under 5% CO<sub>2</sub>. Finally, the cell viability was calculated by MTT assay.

#### The sample preparation for ICP-MS characterization

The samples were prepared according to the method of Ma et al<sup>[3]</sup>. The Fe element content of the Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and MNQDNCs/JMP was measured by dissolving the samples in a plastic container containing HF and HNO<sub>3</sub> (1 : 1, v/v) aqueous solution, respectively, as well as the Zn element content of CdZnSeS QDs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and MNQDNCs/JMP. Then the samples were examined using an inductively coupled plasma-mass spectrometry (ICP-MS).

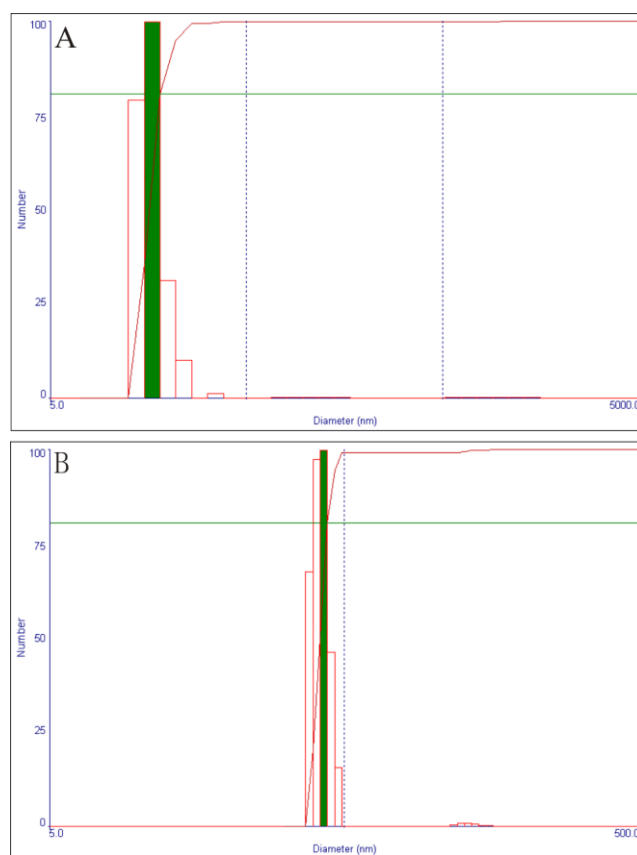


Figure S1. Size distribution of nanoparticles in deionized water measured by the particle size analyzer:  
A: QDs@PSMA; B: MNQDNCs. Both the two samples were drawn through a syringe filter  
(pore size 0.22  $\mu\text{m}$ ).

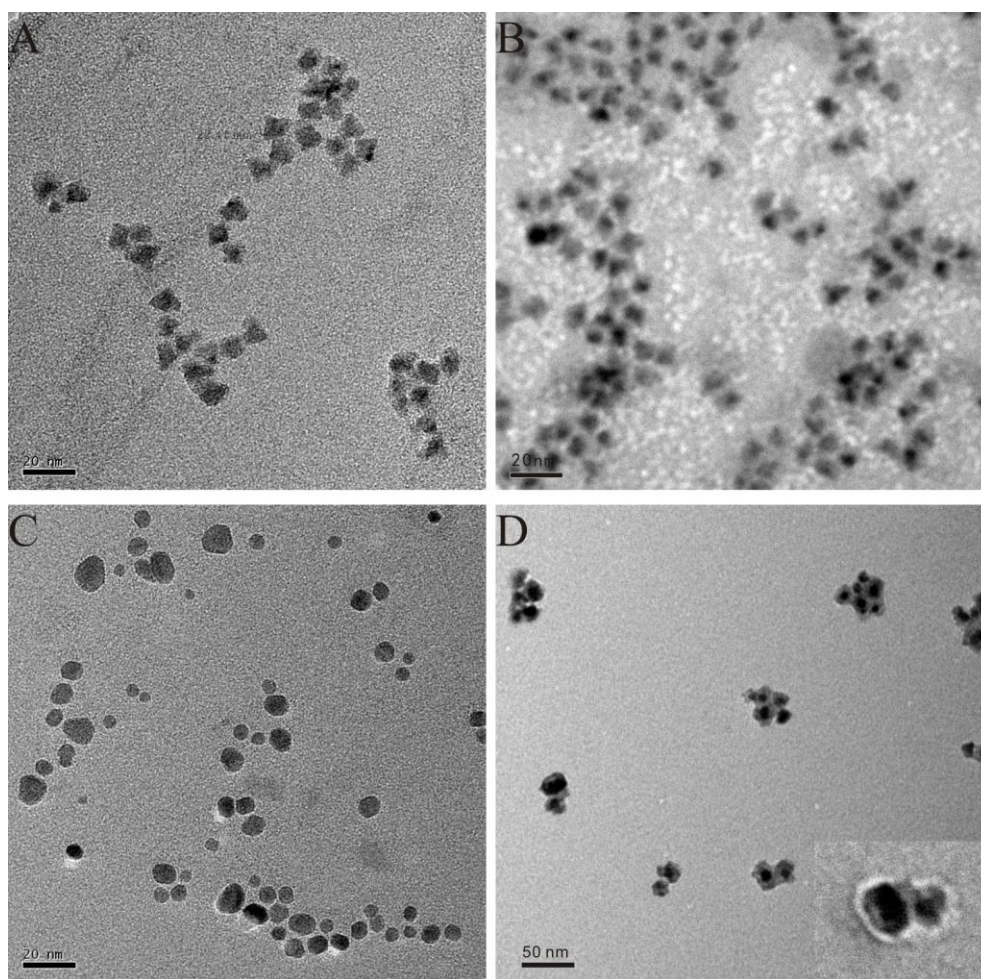


Figure S2. TEM images of CdZnSeS QDs (A), QDs @ PSMA (B), Fe<sub>3</sub>O<sub>4</sub> (C), MNQDNCs (D).

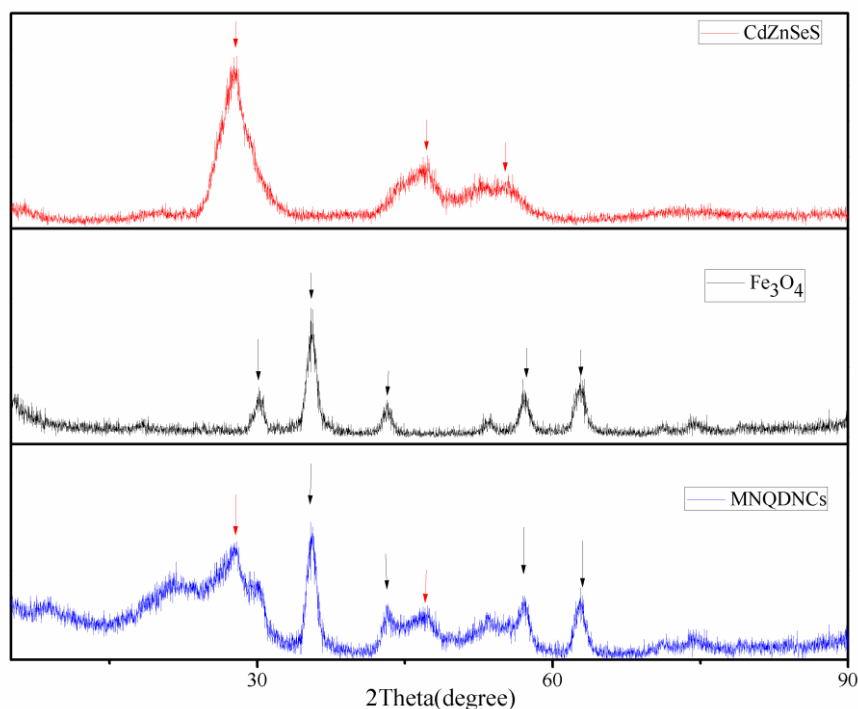


Figure S3. X-ray diffraction patterns of CdZnSeS QDs, Fe<sub>3</sub>O<sub>4</sub> nanoparticles and MNQDNCs. There were obvious diffraction peaks from CdZnSeS QDs and Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the sample of MNQDNCs, The results confirmed that CdZnSeS QDs and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were successfully combined into MNQDNCs. ( ↓ diffraction peak of CdZnSeS QDs; ↓ diffraction peak of Fe<sub>3</sub>O<sub>4</sub> nanoparticles).

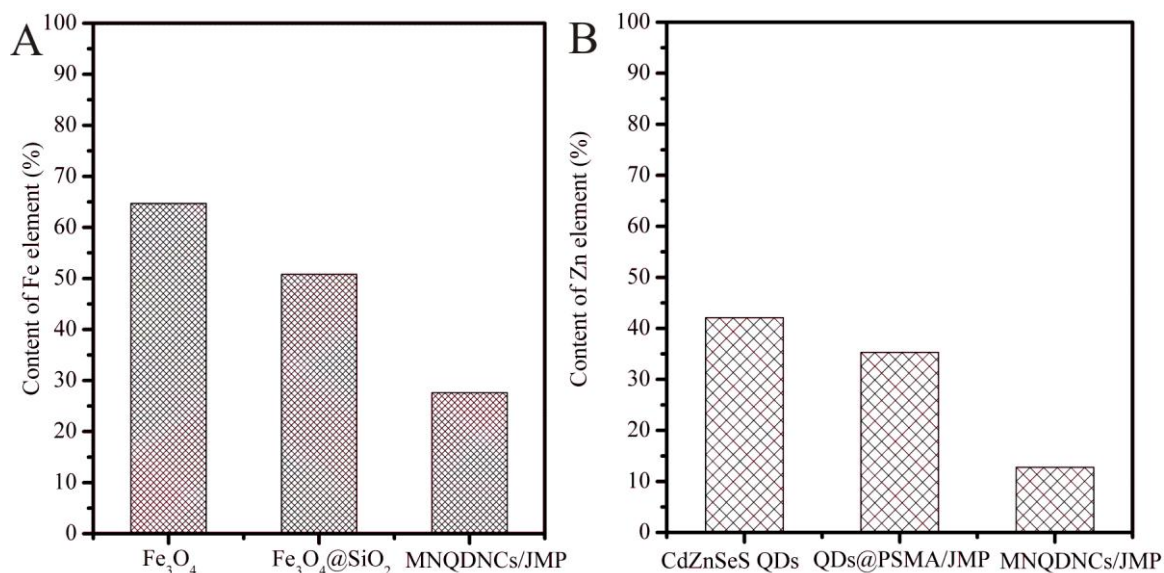


Figure S4. A: the content of Fe element in Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and MNQDNCs/JMP; B: the content of Zn element in CdZnSeS QDs, QDs@PSMA/JMP and MNQDNCs/JMP. The weight proportion of MNs and QDs particles in MNQDNCs/JMP was 42.1:30.9.

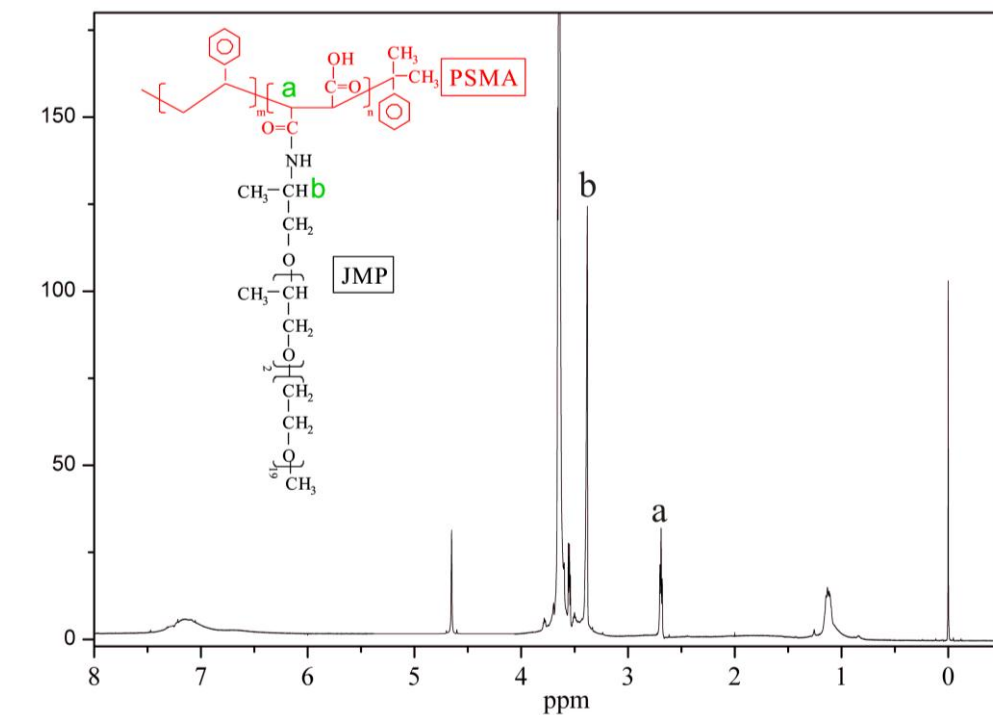


Figure S5.  $^1\text{H}$  NMR spectrum of QDs@PSMA/JMP in  $\text{D}_2\text{O}$ . The peak at 2.68 ppm was related to CH groups (a) from JMP, and the peak at 3.37 ppm was due to CH groups (b) of JMP. Compared the peak area of (a) and (b), it can be estimated that about 70.4% of the maleic anhydride groups from PSMA were ring opened by JMP. (The Sigma-Aldrich product contains 68 wt% styrene and 32 wt% maleic anhydride groups in the polymer chain. Therefore 1  $\mu\text{mol}$  PSMA contains 5.4  $\mu\text{mol}$  maleic anhydride groups.)

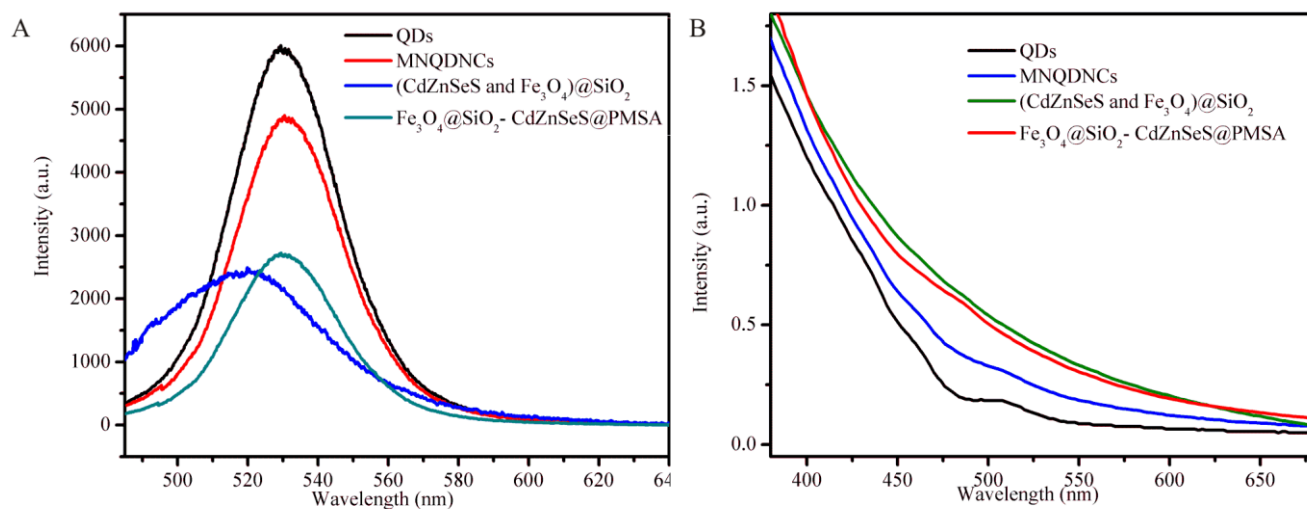


Figure S6. The PL and UV spectra of QDs and magnetic and fluorescent bifunctional nanocomposites prepared by different methods: ring-opening reaction (MNQDNCs), co-encapsulation by  $\text{SiO}_2$  ((CdZnSeS and  $\text{Fe}_3\text{O}_4$ )@ $\text{SiO}_2$ ), CdZnSeS@PSMA conjugating with  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  by coupling agents ( $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ -CdZnSeS@PSMA). The samples prepared by the three methods were purified all by magnetic separation with the same amount of  $\text{Fe}_3\text{O}_4$  nanoparticles.



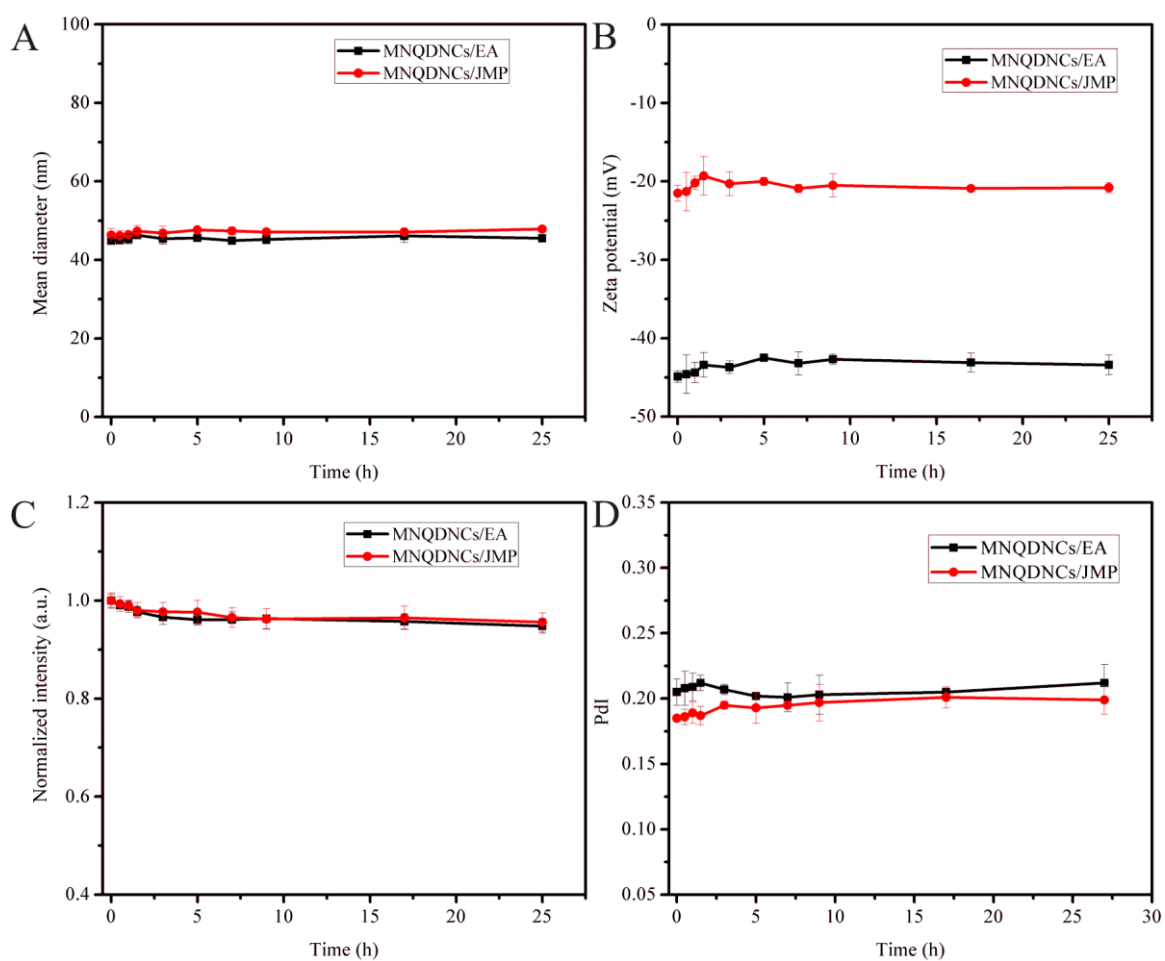


Figure S7. The mean diameter (A), zeta potential (B), fluorescence intensity (C) and PDI (D) of MNQDNCs /EA and MNQDNCs /JMP in PBS at 37 °C at different time.

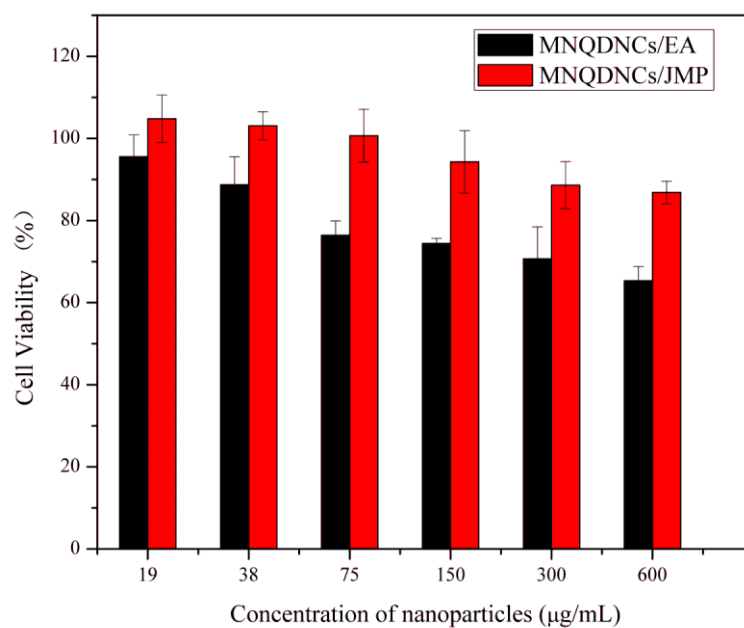


Figure S8. Cytotoxicity of MNQDNCs/JMP and MNQDNCs/EA on Hela cell lines using the MTT assay.

1. M. Darbandi, R. Thomann and T. Nann, *Chemistry of Materials*, 2005, 17, 5720-5725.
2. B. Zhang, B. Chen, Y. Wang, F. Guo, Z. Li and D. Shi, *Journal of Colloid and Interface Science*, 2011, 353, 426-432.
3. L. Gai, L. Zhi, L.Y. Hou, H. Jiang, X. Han and W. Ma, *Journal of Physics D: Applied Physics*, 2010, 43, 445001.