**Supporting Information for**

# Fabrication and Properties of Supramolecular Hybrid Hydrogel Doped with CdTe Quantum Dots

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**S1. Supplemental Data for Colloidal QDs Solution.**

**Table S1.** The feed composition for the preparation of QD colloid solution

| Sample | PEG-PCL-SH / % | QDs [a] / mmol•L$^{-1}$ | Reaction time / h |
|---|---|---|---|
| 1.0%-Sol | 1.0 | 3.0 | 1.0 |
| 2.5%-Sol | 2.5 | 3.0 | 1.0 |
| 5.0%-Sol | 5.0 | 3.0 | 1.0 |
| 2# - 2.5% P | 2.5 | 3.0 | 1.0 |
| 1# - 0.5 T | 2.5 | 3.0 | 0.5 |
| 1# - 1T | 2.5 | 3.0 | 1.0 |
| 1# - 4 T | 2.5 | 3.0 | 4.0 |
| 1# - 1.5 QDs | 2.5 | 1.5 | 1.0 |
| 1# - 3 QDs | 2.5 | 3.0 | 1.0 |
| 1# - 6 QDs | 2.5 | 6.0 | 1.0 |

[a] Calculated by the Cd element in the system.

1#: QDs were modified with $PEG_{114}$-$PCL_{13}$-SH; 2#: $PEG_{114}$-$PCL_{13}$-SH.

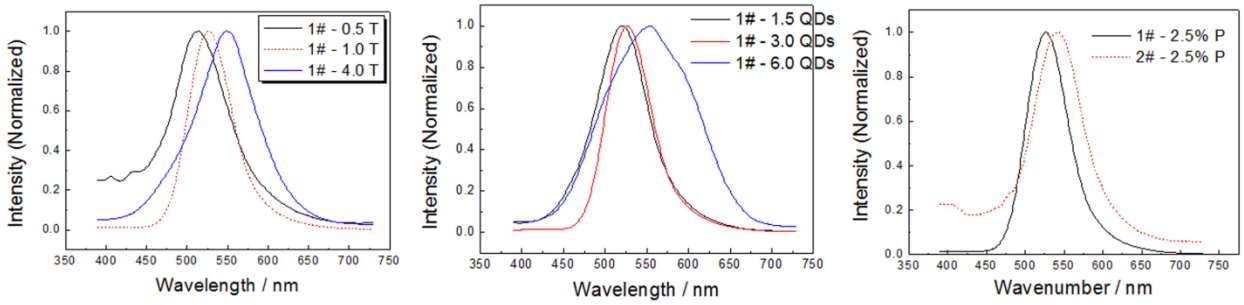



**Figure S1.** Photoluminescence spectra of a series of colloidal CdTe QDs modified with PEG-PCL-SH prepared at different conditions. The sample information is listed in Table S1.

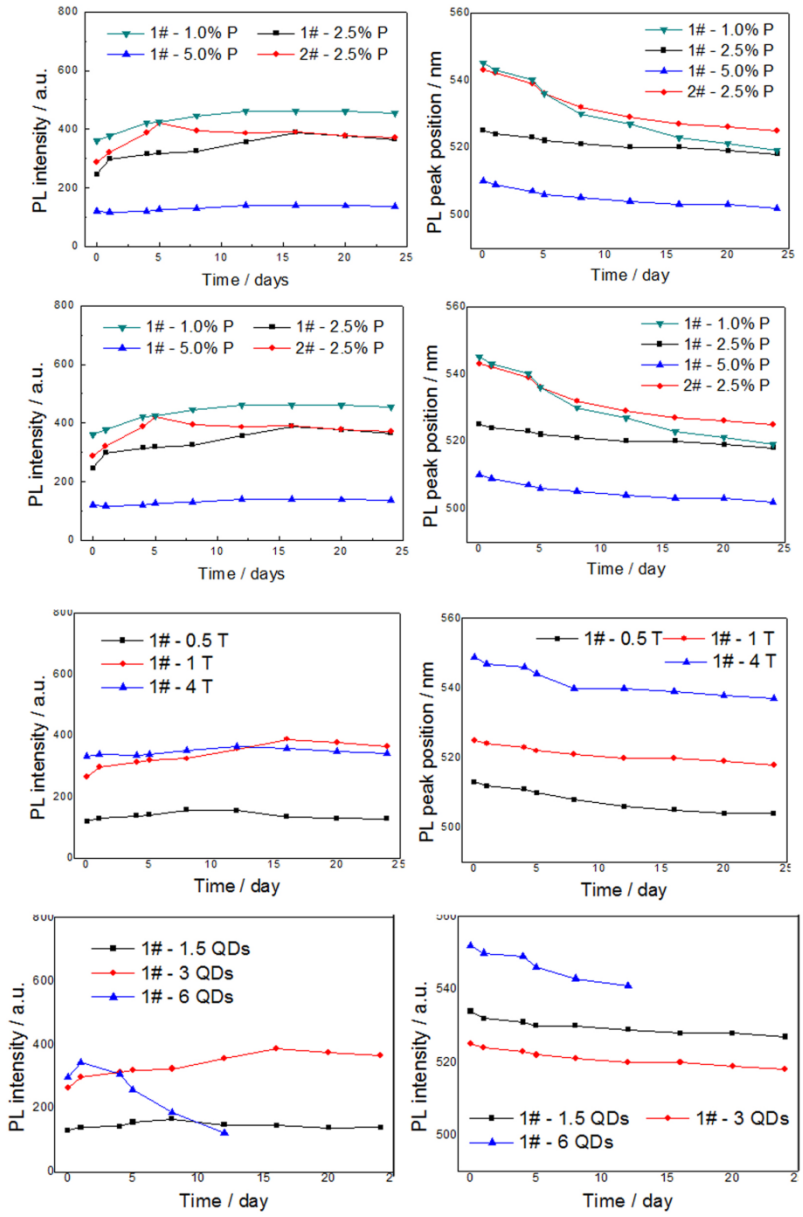



**Figure S2.** Emission peak positions and fluorescent intensities as a function of storage time. The sample information is listed in Table S1.

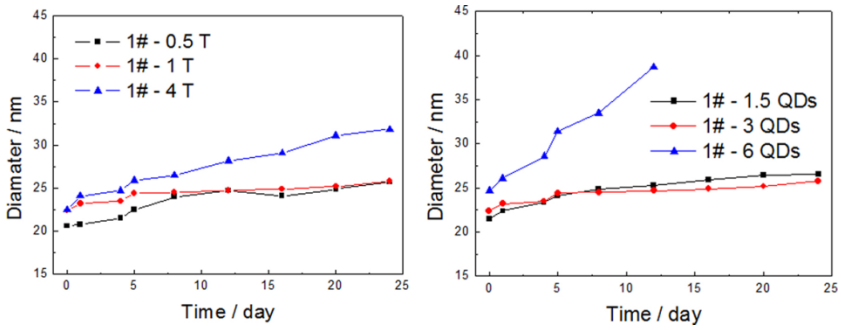



**Figure S3.** Particle sizes as a function of storage time. The sample information is listed in Table S1.

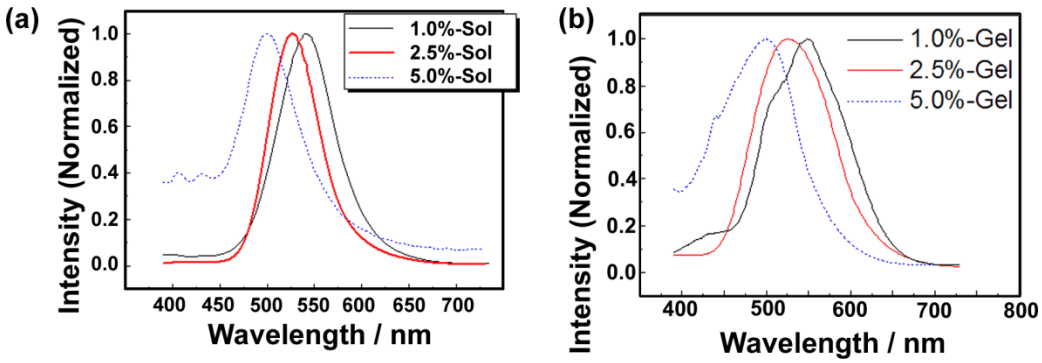
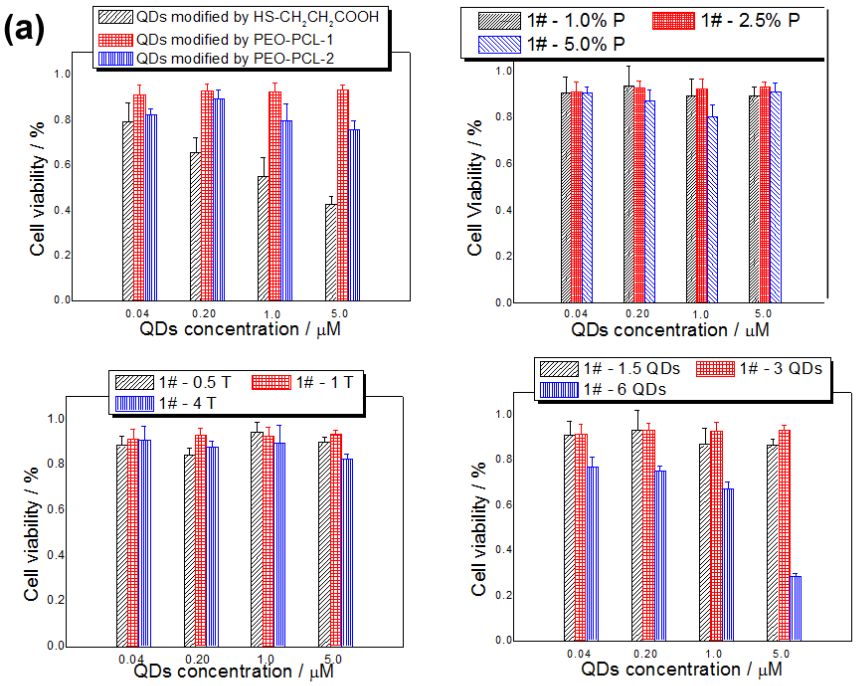


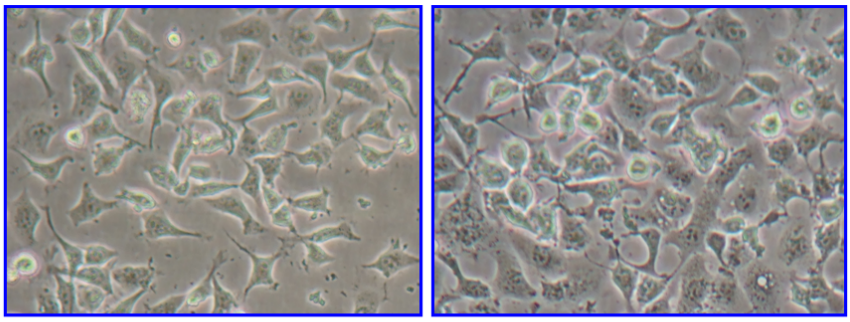

**Figure S4.** (a) Photoluminescence spectra of a series of colloidal CdTe QDs modified with PEG-PCL-SH at different polymer concentration. (b) Photoluminescence spectra of a series of hydrogel doped with colloidal CdTe QDs.

In addition to stabilize the CdTe QDs, the amphiphilic polymer PEG-PCL-SH provides biocompatible interface for the CdTe QDs that would effectively reduces the cytotoxicity of the QDs. The aggregation of colloidal CdTe QDs is likely to impair the proliferation and growth of biological cells. The PEG-PCL-SH effectively stabilize the CdTe nanocrystals preventing their aggregation as shown in main text Figure 3e. The viability of Hep2 cells treated with different concentrations of colloidal QDs was evaluated using MTT assay. As shown in Figure S5a, Hep2 cell viability was observed to be higher than 80% after incubation with 2.5%-Sol and 5.0%-Sol for 24 h. In contrast, cell viability was significantly lower when they were treated with CdTe QDs modified with small molecule-thiohydracrylic acid. This result indicates that the amphiphilic polymer PEG-PCL-SH provided a thicker shell to encapsulate the CdTe QDs and

effectively prevented the oxidation of CdTe nanocrystals and hence reduced the cytotoxicity. The cell morphology of Hep2 cells treated with 0.2 μM 2.5%-Sol was shown in Figure S5b, where the Hep2 cells were observed to spread and proliferate normally.

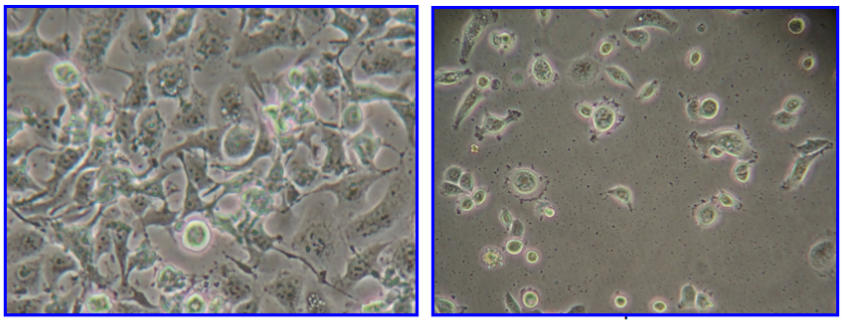



(b)



1# - 2.5% P of 0.20 μM

QDs modified by thiohydracrylic acid of 0.20 μM



QDs modified by thiohydracrylic acid of 1.0 μM

1# - 2.5% P of 5.0 μM

**Figure S5.** (a) Cell viability treated with colloidal QDs determined with MTT assay (n=5). (b) Cell morphology of Hep2 cells treated with 2.5%-Sol. The samples information is listed in Table S1.

Information for cell experiments: Hep2 cell line was cultured in 200 µl DMEM supplemented with 10% fetal bovine serum and 1% antibiotics. Cells were cultured at 37° C and 5% $CO_2$ in 96-wells plate with a density of 4000 cells/well. After incubation for 12 hours, 50 µl colloidal QD solution was added to the cells, and the samples were incubated for another 12 hours. Cell viability was then assessed using MTT cell proliferation assay kits (Sigma). For QDs uptake experiment, the cells were treated with 50 µl QDs solution of 2.5%-Sol with a concentration of 0.2 µM and were incubated for 24 hours. The medium were then replaced with fresh medium and the results were studied with epifluorescence microscope.

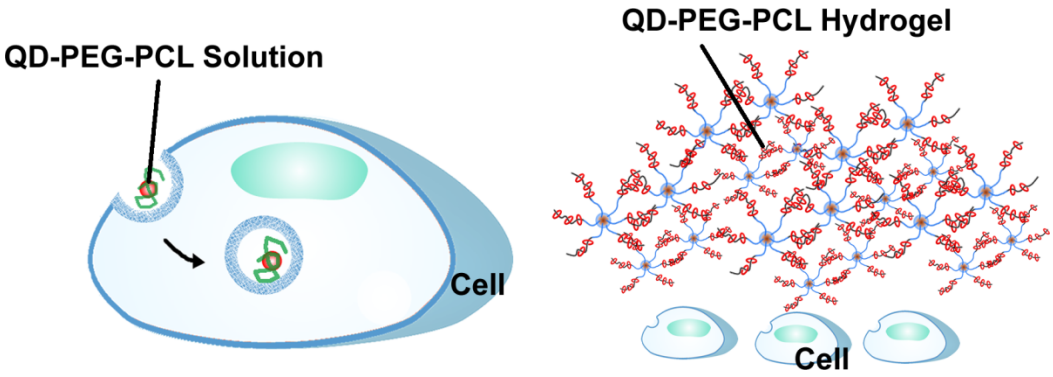



**Figure S6.** Illustration of the cell-interface between QD-PEG-PCL solution with cell and QD-PEG-PCL gel with cell.

QD-PEG-PCL solution has very different cell-interface compared to QD-PEG-PCL gel (Figure S6). Colloidal QD-PEG-PCL was able to get into cell cytoplasm through endocytosis mechanism, while cross-linked hydrogel can only stay on the cell surface. Therefore, colloidal solution is generally more toxic than the hydrogel form, since those composite get into cell interior and directly exposed to the cell's internal environment, while the hydrogel only acts on the cell surface. When the polymer segment released from the hydrogel matrix, it is reduced to the QD-PEG-PCL solution form, and it can be internalized by the cells as well. In this case, the

amount of free QD-PEG-PCL in solution is much lower than the pure QD-PEG-PCL solution since the released polymer concentration tends to be lower. Therefore the cytotoxicity of hydrogel can be expected to be lower than the QD-PEG-PCL solution.