Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

Supporting Information:

Water-Soluble Nanocrystals through Dual-Interaction Ligands

Huimeng Wu,[1] Haizhen Zhu,[2] Jiaqi Zhuang,[1] Shuo Yang,[1] Chen Liu[2] and Y. Charles Cao[1]*

[1]Department of Chemistry, and [2]Department of Pathology,
University of Florida, Gainesville, FL 32611

Fax: 1-352-392-0588; cao@chem.ufl.edu

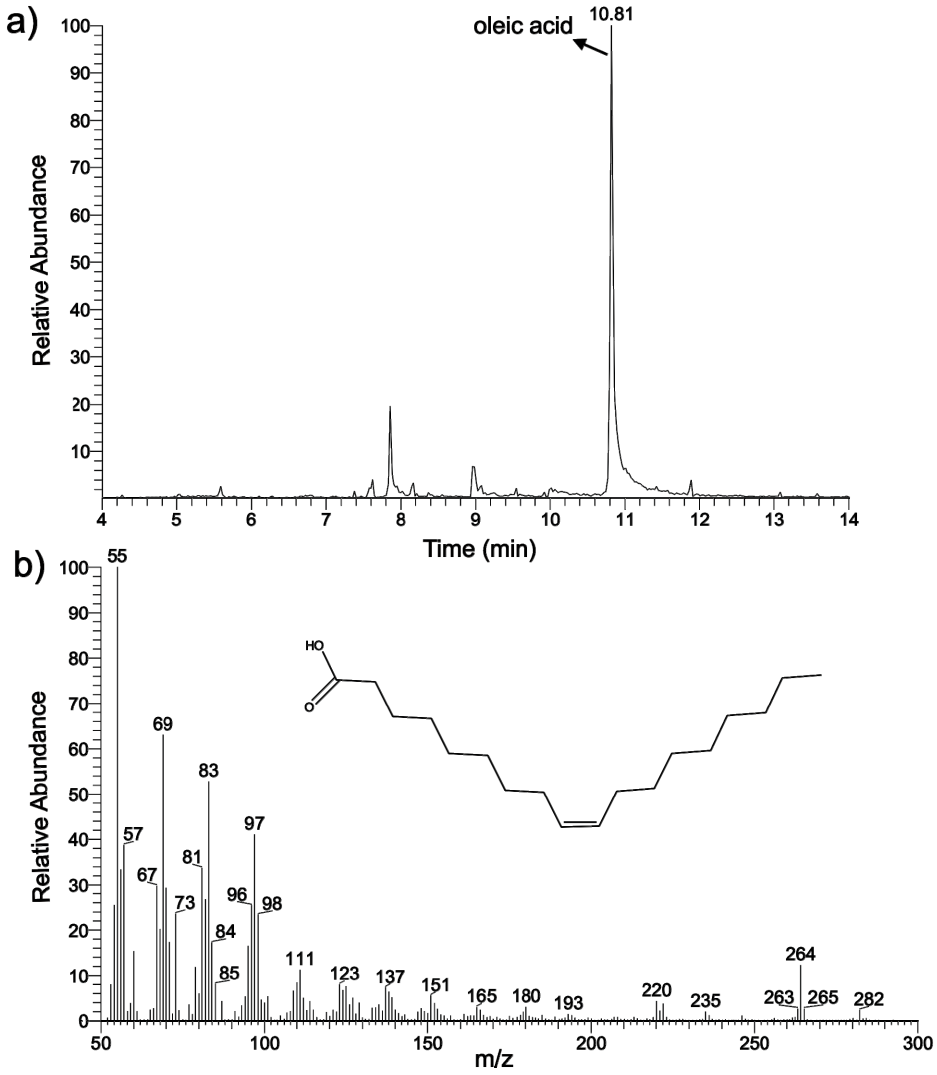


Figure S1. Gas-chromatography mass spectrometry (GC-MS): (a) a gas chromatogram of a solution with the ligands from TD_{20}-D-functionalized Fe_3O_4 nanocrystals; and (b) a mass spectrum of the compound with a retention time of 10.81 min in the gas chromatogram. This spectrum is nearly identical to the NIST standard mass spectrum of oleic acid.[SI] The sample was prepared as follows: TD_{20}-D-functionalized Fe_3O_4 nanocrystals (~15 mg) were dissolved by HCl (10 M, 1 mL), and then water and excess HCl were evaporated from the solution using a rotary evaporator. The resulting yellow, oily residue was dissolved in methanol (1 mL) for the GC-MS measurements.

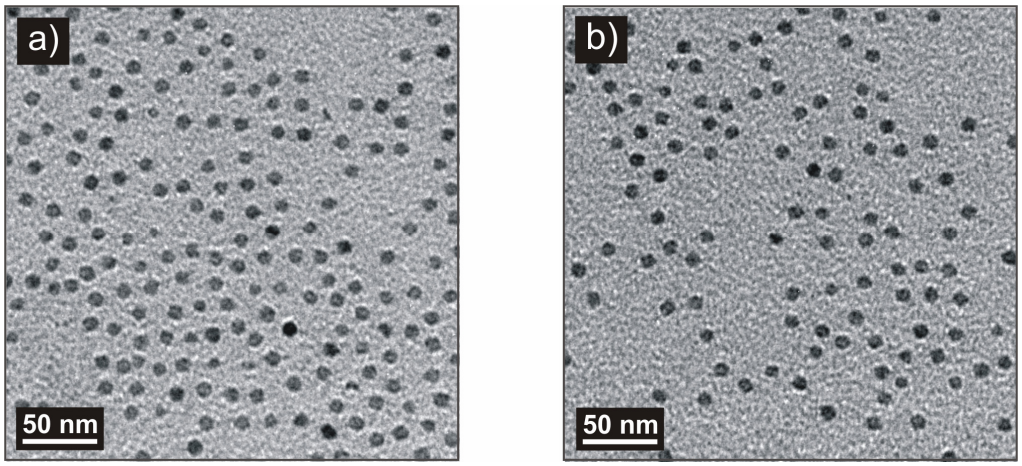


Figure S2. TEM images of TD_{20}-D-capped Fe_3O_4 nanocrystals from aqueous solutions at (a) pH 7 and (b) pH 2 for 2h.

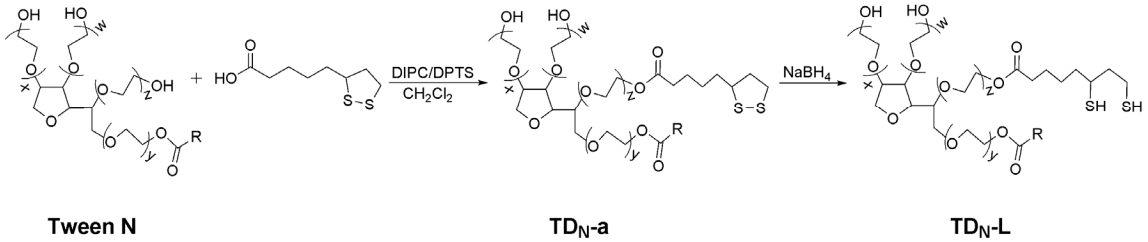
Synthesis and Method:

1. Chemicals. Butylamine (99%), dimethylaminopyridine (DMAP, 99%), dopamine hydrochloride, hexamethyl-disilathiane ($(TMS)_2S$), lipoic acid (≥ 99%), 1-methyl-2-pyrrolidinone (NPA, ≥ 99%), *N,N'*-diisopropyl carbodiimide (DIPC, 99%), iron chloride ($FeCl_3 \cdot 6H_2O$, 98%), 1-octadecene (ODE, 90%), octadecylamine (ODA, 97%), oleic acid (OA, 90%), *p*-toluenesulfonic acid monohydrate (98%), rhodamine 6G (99%), tributylphosphine (TBP, 97%), trioctylphosphine oxide (TOPO, 99%), polyethylene glycol sorbitan monolaurate (Tween-20), polyethylene glycol sorbitan monolaurate (Tween-40), polyethylene glycol sorbitan monostearate (Tween-60) and polyethylene glycol sorbitan monooleate (Tween-80) were purchased from Aldrich. Cadmium oxide (CdO, 99.998%), selenium (Se, 99.99%), dodecyl trimethylammonium bromide (DTAB, 97%) were purchased from Alfa Aesar. Sodium oleate (95%) was purchased from TCI. Nanopure water (18.2 MΩ·cm) was prepared by a Barnstead Nanopure Diamond system. All the other solvents were purchased from Fisher Scientific International Inc.

2. Synthesis of Tween-derivatives (TDs)

4-(*N,N'*-Dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared by mixing THF solutions of DMAP (2 M, 50 mL) and *p*-toluenesulfonic acid monohydrate (2 M, 50 mL) at room temperature with stirring. The resulting precipitate was filtered and dried under vacuum.[*S2*]

1) TD_N-L (Dihyolipoic acid-functionalized Tweens)



w + x + y + z = 20, N = 20, 40, 60, 80
Tween 20: R = $C_{11}H_{23}$; Tween 40: R = $C_{15}H_{31}$; Tween 60: R = $C_{17}H_{35}$; Tween 80: R = $C_7H_{14}CH{=}CHC_8H_{17}$

TD_{20}-a:[5-(1,2-Dithiolan-3-yl)-1-oxopentyl]polyethylene glycol sorbitan monolaurate. Tween-20 (4.91 g, 4.0 mmol), lipoic acid (0.83 g, 4.0 mmol), and DPTS (1.37 g, 4.4 mmol) were mixed in CH_2Cl_2 (20 mL) and stirred for several minutes at room temperature. Then, DIPC (0.63 mL, 4.4 mmol) was added to the mixture. After being stirred at room temperature overnight, the reaction mixture was washed with water (30 mL) four times. The organic phase was dried over magnesium sulfate ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluents: ethyl acetate/hexane 9:1 and chloroform/methanol 9:10). Yield: 88%. ^{1}H-NMR (300 MHz, $CDCl_3$, Figure S3): δ_a 0.88 (t, 3H), δ_b 1.25 (m, 16H), δ_c 1.47 (m, 2H), δ_d 1.63 (m, 6H), δ_e 1.90 (m, 1H), δ_f 2.33 (m, 4H), δ_g 2.45 (m,1H), δ_h 3.13 (m, 3H), δ_i 3.63 (m, 82H), δ_j 4.21 (m, 4H), δ_k 4.56 (m, 2H).

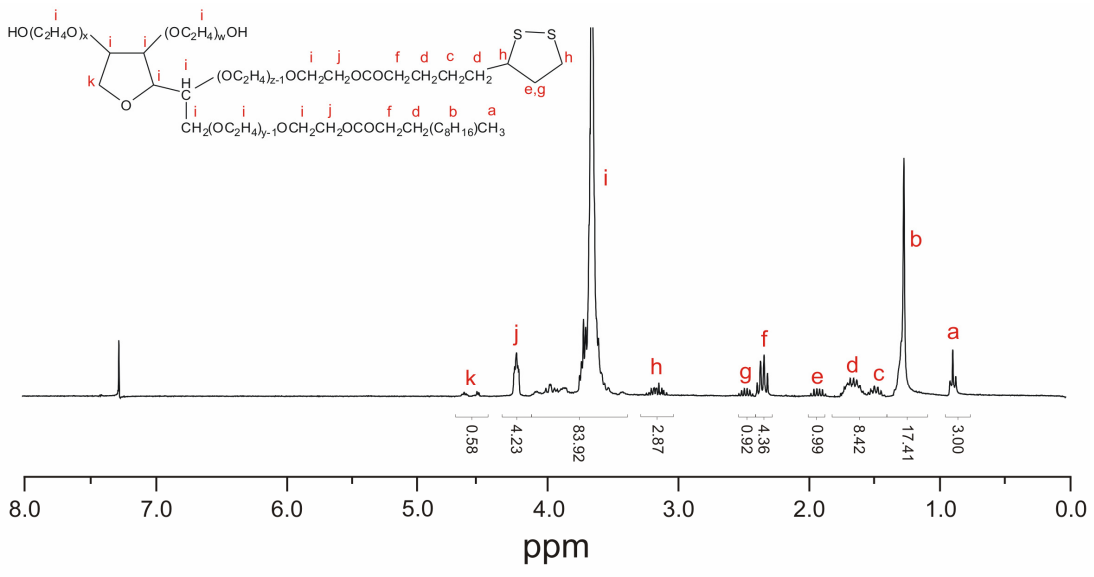


Figure S3. ^{1}H-NMR of compound TD_{20}-a

TD_{20}-L: (6,8-Dimercapto-1-oxoocty)polyethylene glycol sorbitan monolaurate. TD_{20}-a (4.96 g, 3.5 mmol) was dissolved in a mixture of EtOH/water (50 mL, 1:4). Then $NaBH_4$ (0.23 g, 6.0 mmol) was slowly added. The reaction mixture was stirred for 2 h until the

solution became colorless. Then, the solution was diluted with water (50 mL) and extracted with $CHCl_3$ (50 mL) five times. The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give a white oily product. Yield: 82%. ^{1}H-NMR (300 MHz, $CDCl_3$, Figure S4): δ_a 0.88 (t, 3H), δ_b 1.24 (m, 16H), δ_c 1.47 (m, 2H), δ_d 1.63 (m, 6H), δ_e 1.90 (m, 1H), δ_f 2.33 (m, 4H), δ_g 2.92 (m,1H), δ_h 2.70 (m, 3H), δ_i 3.63 (m, 82H), δ_j 4.21 (m, 4H), δ_k 4.56 (m, 2H).

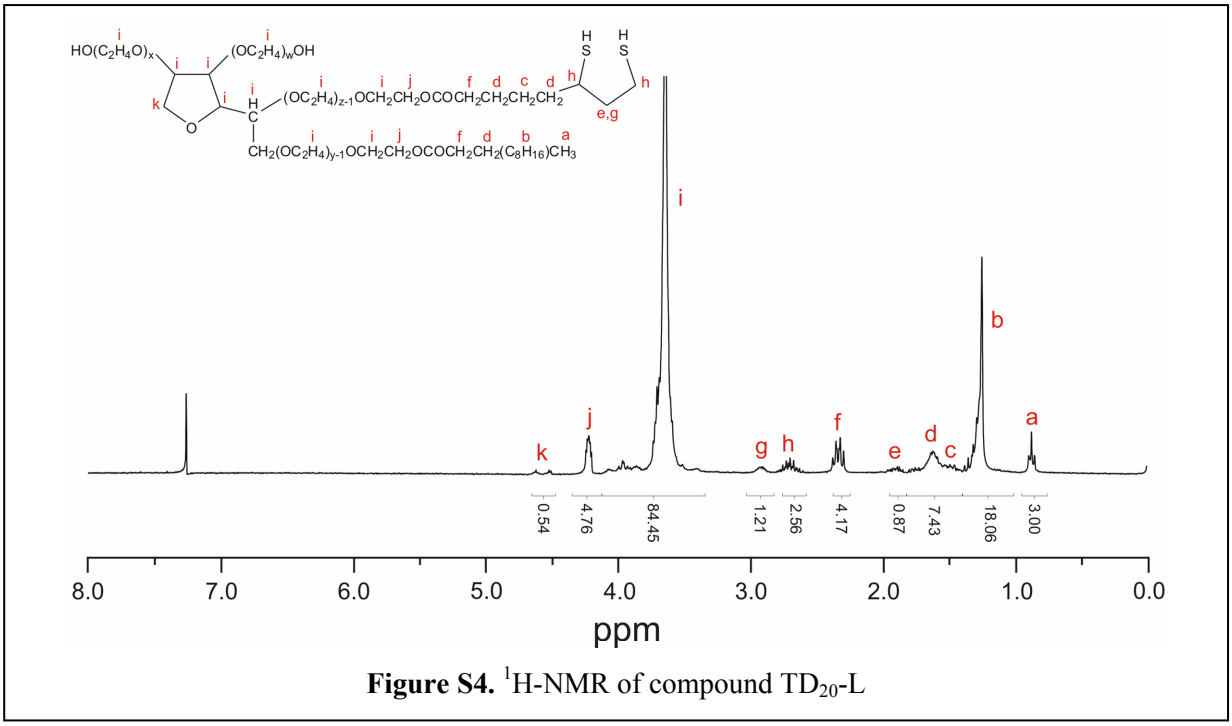


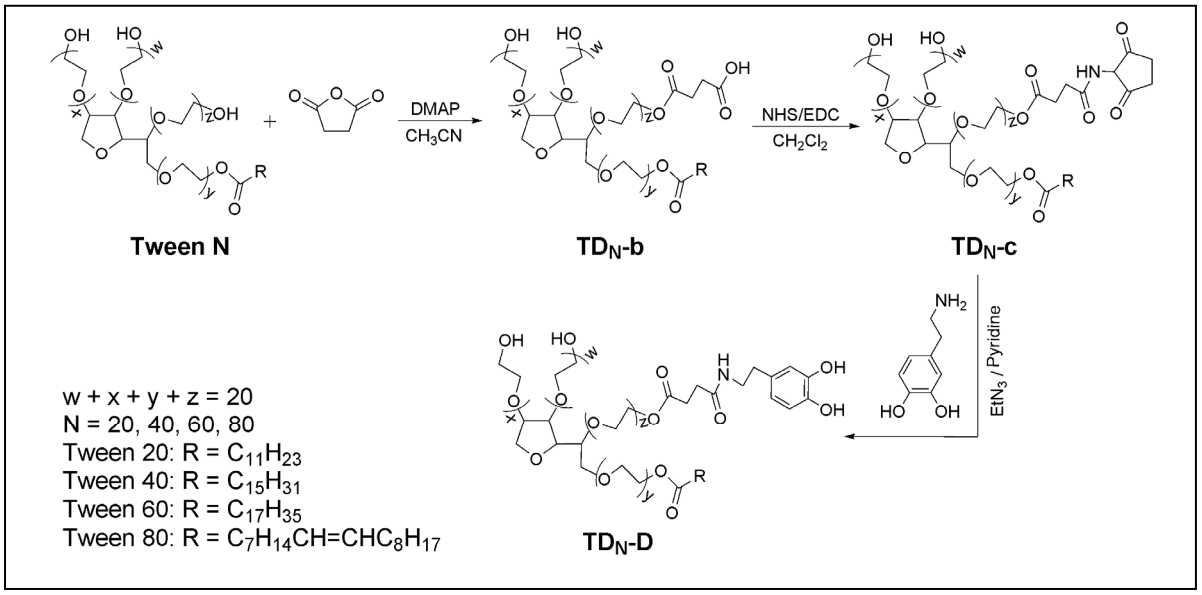
Figure S4. ^{1}H-NMR of compound TD_{20}-L

TD_{40}-L: (6,8-Dimercapto-1-oxoocty)polyethylene glycol sorbitan monopalmitate was synthesized using similar conditions as those for the synthesis of TD_{20}-L. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.24 (m, 24H), 1.47 (m, 2H), 1.63 (m, 6H), 1.90 (m, 1H), 2.33 (m, 4H), 2.92 (m,1H), 2.70 (m, 3H), 3.63 (m, 82H), 4.21 (m, 4H), 4.56 (m, 2H).

TD_{60}-L: (6,8-Dimercapto-1-oxoocty)polyethylene glycol sorbitan monostearate was synthesized using similar conditions as those for the synthesis of TD_{20}-L. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.24 (m, 28H), 1.47 (m, 2H), 1.63 (m, 6H), 1.90 (m, 1H), 2.33 (m, 4H), 2.92 (m,1H), 2.70 (m, 3H), 3.63 (m, 82H), 4.21 (m, 4H), 4.56 (m, 2H).

TD_{80}-L: (6,8-Dimercapto-1-oxoocty)polyethylene glycol sorbitan monooleate was synthesized using similar conditions as those for the synthesis of TD_{20}-L. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.24 (m, 20H), 1.47 (m, 2H), 1.63 (m, 6H), 1.90 (m, 1H), 2.33 (m, 4H), 2.92 (m,1H), 2.70 (m, 3H), 3.63 (m, 82H), 4.21 (m, 4H), 4.56 (m, 2H), 5.34(t, 2H).

2) TD_N-D (Dopamine-functionalized Tweens)



TD_{20}-b: (3-Carboxy-1-oxopropyl)polyethylene glycol sorbitan monolaurate. A mixture of Tween-20 (4.91 g, 4.0 mmol), succinic anhydride (0.41 g, 4.0 mmol) and DMAP (18 mg, 0.15 mmol) in 20 mL of dry acetonitrile was refluxed overnight with stirring. Then the solution was cooled to room temperature. The solvent was evaporated under reduced pressure. Then, the oily residue was dissolved in $CHCl_3$ (100 mL) and washed with HCl (1 M, 40 mL) three times and then water (60 mL) three times. The organic phase was dried over $MgSO_4$ and filtered. The yellow oily product was obtained after removal of the solvent. Yield: 93%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 0.88 (t, 3H), 1.25 (m, 16H), 1.60 (m, 2H), 2.32 (t, 2H), 2.63 (s, 4H), 3.63 (m, 82H), 4.23 (m, 4H), 4.57 (m, 2H).

TD_{20}-c: [4-[(2,5-Dioxo-1-pyrrolidinyl)oxy]-1,4-dioxobutyl]polyethylene glycol sorbitan monolaurate. TD_{20}-b (4.85 g, 3.7 mmol) and *N*-hydroxysuccinimide (NHS, 0.43 g, 3.7 mmol) were mixed in CH_2Cl_2 (20 mL). Then EDC (0.71 g, 3.7 mmol) was added. After being stirred at room temperature overnight, the reaction mixture was diluted with CH_2Cl_2 (30 mL).[*S3*] Then this solution was washed with HCl (0.1 N, 60 mL) twice and then brine (60 mL) twice. The organic phase was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluents: ethyl acetate/hexane 9:1) and chloroform/methanol 9:1) to give a yellow oily product. Yield: 89%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 0.88 (t, 3H), 1.25 (m, 16H), 1.60 (m, 2H), 2.32 (t, 2H), 2.84 (s, 4H), 2.78(t, 2H), 2.97 (t, 2H), 3.63 (m, 82H), 4.26 (m, 4H), 4.57 (m, 2H).

TD_{20}-D: [[[2-(3,4-Dyhydroxyphenyl)ethyl]amino]carbonyl]polyethylene glycol sorbitan monolaurate. Dopamine hydrochloride (0.63 g, 3.3 mmol) and triethylamine (0.33 g, 3.3 mmol) were mixed in 1mL of pyridine. Then the mixture was added to a solution of TD_{20}-c (4.63 g, 3.3 mmol) in pyridine (10 mL). After being stirred for 2 h, the pyridine and solvent were removed under reduced pressure. The oily residue was dissolved in CH_2Cl_2 (20 mL) and the insoluble solid was filtered away. Then, the solution was washed with water (30 mL) three

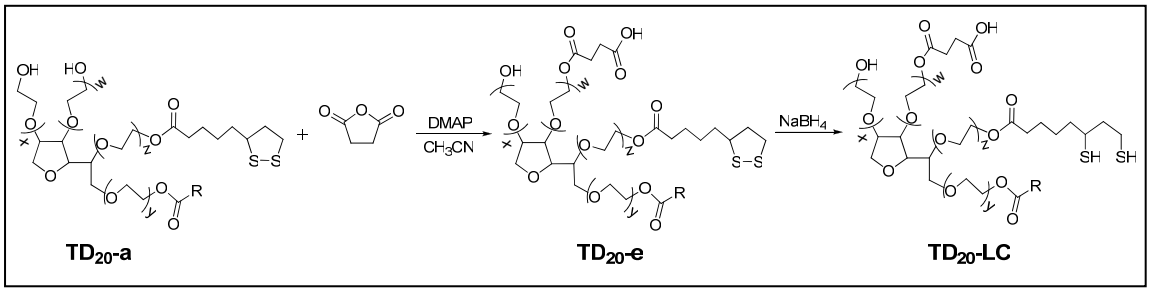
times. The organic phase was dried over $MgSO_4$ and filtered. A dark yellow oily product was obtained after evaporation of the solvent. Yield: 90 %. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), δ_b 1.25 (m, 16H), 1.62 (m, 2H), 2.33 (m, 2H), 2.43 (t, 2H), 2.84 (m, 4H), 3.435 (t, 2H), 3.64 (m, 84H), 4.21 (m, 4H), 4.56 (m, 2H), 6.55 (d, 1H), 6.70 (s, 1H) and 6.79 (d, 1H).

TD_{40}-D: [[[2-(3,4-Dyhydroxyphenyl)ethyl]amino]carbonyl]polyethylene glycol sorbitan monopalmitate was synthesized using similar conditions as those for the synthesis of TD_{20}-D. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.25 (m, 24H), 1.62 (m, 2H), 2.33 (m, 2H), 2.43 (t, 2H), 2.84 (m, 4H), 3.435 (t, 2H), 3.64 (m, 84H), 4.21 (m, 4H), 4.56 (m, 2H), 6.55 (d, 1H), 6.70 (s, 1H) and 6.79 (d, 1H).

TD_{60}-D: [[[2-(3,4-Dyhydroxyphenyl)ethyl]amino]carbonyl]polyethylene glycol sorbitan monolaurate was synthesized using similar conditions as those for the synthesis of TD_{20}-D. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.25 (m, 26H), (m, 2H), 2.33 (m, 2H), 2.43 (t, 2H), 2.84 (m, 4H), 3.435 (t, 2H), 3.64 (m, 84H), 4.21 (m, 4H), 4.56 (m, 2H), 6.55 (d, 1H), 6.70 (s, 1H) and 6.79 (d, 1H).

TD_{80}-D: [[[2-(3,4-Dyhydroxyphenyl)ethyl]amino]carbonyl]polyethylene glycol sorbitan monolaurate. was synthesized using similar conditions as those for the synthesis of TD_{20}-D. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H),1.25 (m, 20H), 1.62 (m, 2H), 1.99 (m, 4H), 2.33 (m, 2H), 2.43 (t, 2H), 2.84 (m, 4H), 3.435 (t, 2H), 3.64 (m, 84H), 4.21 (m, 4H), 4.56 (m, 2H), 5.34 (t, 2H), 6.55 (d, 1H), 6.70 (s, 1H) and 6.79 (d, 1H).

*3) TD_{20}-LC (*carboxyl-group-functionalized *TD_{20}-L)*



TD_{20}-e: α-[5-(1,2-Dithiolan-3-yl)-1-oxopentyl]-ω-(3-carboxy-1-oxopropyl) poly-ethylene glycol sorbitan monolaurate. A mixture of TD_{20}-a (4.96 g, 3.5 mmol), succinic anhydride (0.36 g, 3.5 mmol) and DMAP (18 mg, 0.15 mmol) in dry acetonitrile (20 mL) was refluxed overnight with stirring. Then, the solution was cooled to room temperature. The solvent was evaporated under reduced pressure. The oily residue was dissolved in $CHCl_3$ (10 mL) and washed with HCl solution (1 M, 40 mL) twice and with water (50 mL) twice. The organic phase was dried over $MgSO_4$ and filtered. The yellow oily product was obtained after evaporation of the solvent. Yield: 98%. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.24 (m, 16H), 1.46 (m, 2H), 1.63 (m, 6H), 1.90 (m, 1H), 2.32 (m, 4H), 2.45 (m,1H), 2.65 (2.66, 4H), 3.13 (m, 3H), 3.63 (m, 82H), 4.21 (m, 6H), 4.56 (m, 2H).

TD_{20}-LC:α-[5-(1,2-Dithiolan-3-yl)-1-oxopentyl]-ω-(6,8-dimercapto-1-oxoocty)-polyethylene glycol sorbitan monolaurate. TD_{20}-e (5.14 g, 3.4 mmol) in $NaHCO_3$ aqueous solution (0.25 M, 100 mL) was cooled with an ice bath for 5 minutes. Then $NaBH_4$ (0.53 g, 14 mmol) was added slowly. The reaction mixture was stirred for 2 h until the reaction mixture turned colorless. Then, HCl (6 M, 10 mL) was added to quench the reaction. The mixture was extracted with $CHCl_3$ (50 mL) five times. The combined organic solution was dried over $MgSO_4$ and filtered. A white oily product was obtained after evaporation of the solvent. Yield: 92%. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ (ppm) 0.88 (t, 3H), 1.24 (m, 16H), 1.47 (m, 2H), 1.63 (m, 6H), 1.90 (m, 1H), 2.33 (m, 4H), 2.92 (m,1H), 2.65 (2.66, 4H), 2.70 (m, 3H), 3.63 (m, 82H), 4.21 (m, 6H), 4.56 (m, 2H).

3. Nanocrystal synthesis

1-dodecanethiol-capped 6.6-nm gold nanocrystals were synthesized according to the literature procedure.[*S4*] In a typical synthesis, $AuCl_3$ (0.068 g) was dissolved in a DTAB solution (0.185 g of DTAB in 20 mL of toluene) with ultrasonication to form a dark orange solution. Then a freshly-prepared aqueous solution of $NaBH_4$ (75 μmol) was added dropwise to the solution with vigorous stirring. After 20 minutes, 1-dodecanethiol (1.6 mL) was added and the stirring was continued for 10 minutes. The nanoparticles were precipitated by adding ethanol, and the solid was re-dispersed in toluene (20 mL) in the presence of 1-dodecanethiol (1.6 mL) and refluxed for 30 minutes under nitrogen. The nanocrystals were precipitated from the reaction solution with ethanol (30 mL), isolated by centrifugation and re-dispersed in $CHCl_3$. The resulting nanoparticles have a diameter of 6.6 nm with a standard deviation of 7.0 %.

Oleic-acid-capped 5.8-nm Fe_3O_4 nanocrystals were synthesized according to the literature method.[*S5*]

Oleylamine-capped 5.6-nm CdSe/ZnS core/shell nanocrystals. CdSe/ZnS core/shell nanocrystals were prepared by a two-step procedure consisting of synthesis of CdSe core nanocrystal and growth of ZnS layers. The syntheses were conducted according to the literature method.[*S6*]

4. Preparation of TD-capped water-soluble nanoparticles

Hydrophobic nanoparticles (i.e., Au, Fe_3O_4 or CdSe/ZnS) (25 nmol) and TDs (e.g., TD_N-L, TD_N-D or TD_{20}-LC) (10 μmol) were mixed in $CHCl_3$ (5 mL). The solution was stirred at room temperature for 10 minutes. Then triethylamine (0.05 mL) was added into the mixture. The resulting mixture was stirred further for 10 minutes. After evaporation of the solvent, these nanocrystals were re-dispersed in water. The nanocrystal solution was filtered through a 0.22-μm MCE syringe filter (Fisher Scientific). The excess of TD ligands was washed away with spin filters (Millipore, 10K NMWL, 10000×g, 10 min) for four times. The resulting nanocrystals were re-dispersed in water (pH 7) for further studies.

5. Stability tests

Each stability test was repeated more than five times using the same batch of TD-capped nanocrystals. The sample standard deviation *(S)* and relative standard deviation (σ) were calculated by the following equations, respectively:

$$S=\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i-\bar{x})^2}\ ;\ \text{and}\ \sigma = S / \bar{x}$$

Where x_i is the data of each experiment and $\bar{x}$ is the average value of these experiments. The following is an example.

For example, five sets of DLS data (Figure S5) were obtained from five parallel stability-test experiments. The nanocrystal hydrodynamic size in each experiment is (a) 16.3 nm, (b) 17.8 nm, (c) 17.1 nm (d) 17.3 nm and (e) 17.0 nm. So the average size of these five experiments was 17.1 nm ± 0.54 nm and σ = 3.2%, as calculated by the above equations.

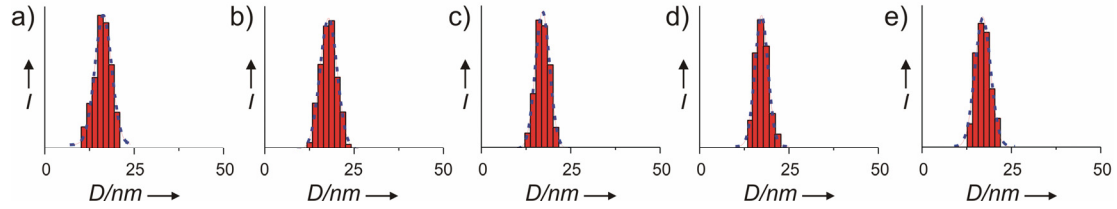


Figure S5. DLS data of TD_{20}-L-functionalized 6.6-nm Au nanocrystals from five parallel thermal-stability-test experiments (at 100 ^{o}C and pH 6.5 for 120 min).

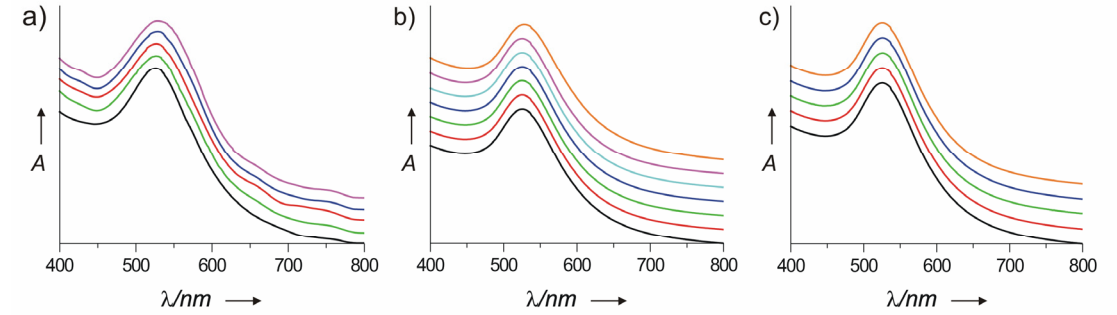


Figure S6. UV-Vis spectra for the stability tests of TD_{20}-L-functionalized Au nanocrystals: (a) thermal stability test at 100 ^{o}C as a function of time: Black: 0 h, Red: 1 h, Green: 2 h, Blue: 3 h and Magenta: 4 h; (b) stability as a function of pH values. Black: pH 1; Red: pH 2, Green: pH 3, Blue: pH 7, Cyan: pH 12, Magenta: pH 13 and Orange: pH 14; (c) stability as a function of NaCl concentration. Black: 0 M, Red: 1 M, Green: 2 M, Blue: 3.5 M and Orange: 5 M.

6. Antibody-functionalized CdSe/ZnS nanocrystal QDs

Hydrophilic CdSe/ZnS QDs with a diameter of 5.6 nm (δ ~ 8.0 %) and capped with a mixture of compound TD_{80}-L and TD_{20}-LC (5:1 molar ratio) were prepared as described above. CdSe/ZnS QDs (0.20 nmol) were dissolved in 2-(*N*-morpholino)ethanesulfonic-acid buffer solution (MES buffer, 0.1 M, 150 μL, pH = 6.0). An aqueous solution of 1-ethyl-3-(3-dimethylaminipropopyl) carbodiimide (EDC, 5.0 mg/mL, 50 μL) and an aqueous solution of N-hydroxysulfosuccinimide (Sulfo-NHS, 5.0 mg/mL, 50 μL) were added to the QDs buffer solution. The mixture solution was incubated for 1 h at room temperature with gentle shaking. 2-mercaptoethanol (1.0 μL) was added to the reaction mixture to quench the EDC. Then the excess reducing agent and inactivated cross-linker were removed by filtering through a NAP-5 column. Phosphate Buffered Saline (PBS buffer, pH = 7.4) was used as the elution buffer. The collected QD solution was concentrated to 50 μL by spin filter (10K NMWL, Millpore, 10000×g, 10 min) and re-dissolved in a PBS buffer solution (250 μL, pH 7.4). NS5A-specific mouse monoclonal antibody (100 μg) was added into the QD solution, and resulting mixture was incubated for 2 h at room temperature. Hydroxylamine (0.5 μL) was added to quench the reaction. The mixture was transferred to a spin filter (100K NMWL, Millpore, 10000×g, 10 min) and concentrated to 50 μL. Then PBS buffer solution (200 μL, pH 7.4) was added and the mixture was spun again. The washing step was repeated 2 times to remove thoroughly the free antibodies. Finally, the purified antibody-functionalized QDs (0.15 nmol) were re-dispersed in a PBS buffer solution (450 μL, pH 7.4). Sodium azide was added to the solution of antibody-functionaled QDs (with a concentration of 0.01 % (w/v as a preservative).

7. Immunostaining tests

FCA1 HCV replicon cells were grown on glass coverslips for 24 h, and the cells were fixed in an ethanol solution with 5% acetic acid at -20 ^{o}C overnight. The fixed cells were washed with PBS (pH 7.4) at room temperature twice (5 minutes each time), and the cells were blocked by 1:50 normal goat serum for 30 min at room temperature. Then the cells were incubated with NS5A-specific-antibody functionalized QDs (50 nM, 0.20 mL) at room temperature for 1 h. After the cells were washed with PBS (pH 7.4) for 3 times (5 minutes each), the nuclei of the cells were counterstained with DAPI (4′,6-diamidino-2-phenylindole,Vector Laboratories Inc, Burlingame, CA) as an internal reference, and the extra DAPI was washed away with PBS (pH 7.4). Finally, the FCA1 cells were examined under a fluorescence microscope (Olympus BX51, Olympus Imaging America Inc, Center Valley, PA).

In a control test, TD-capped DQs (with the ratio of TD_{80}-L and TD_{20}-LC = 5:1), which were not functionalized with NS5A-specific antibody, were used for staining FCA1 cells.

Histograms of fluorescent images show the mean pixel intensities. The intensity ratio of blue channel (from DAPI) and red channel (from QDs) were calculated for each cell, and more than 300 cells were analyzed.

8. Other measurements

1) ^{1}H-NMR measurements

^{1}H-NMR spectra were recorded using a Varian Mercury NMR Spectrometer (300 MHz). The samples were prepared by adding aliquots of products (10 mg) into a deuterated solvent ($CDCl_3$, ~ 0.6 mL).

2) Fluorescence quantum yields (QY) determination

Fluorescent spectra were measured using a spectrofluorometer (Fluorolog-3, Horiba Jobin Yvon, Irvine, CA). Room-temperature fluorescence QY of the CdSe/ZnS core/shell QDs was determined by using the literature method.[S7] LD690 (63% QY) was used as reference and excitation wavelength was 500 nm.

3) Dynamic light scattering

The nanoparticle aqueous solutions were filtered through a 0.22-μm MCE syringe filter (Fisher Scientific) first. The hydrodynamic sizes of nanocrystals were obtained from a dynamic light scattering (DLS) (Brookhaven Instruments Corporation, Holtsville, NY) at 25 ^{o}C.

4) TEM measurements

TEM measurements were performed on a JEOL 200CX operated at 200 kV. The specimens were prepared as follows: a particle solution (10 μL) was dropped onto a 200-mesh copper grid, and dried overnight at ambient conditions.

References

S1. NIST MS Search 2.0 (http://chemdata.nist.gov).
S2. H. Wu, Y. Yang, Y. C. Cao, *J. Am. Chem. Soc.* **2006**, *128*, 16522.
S3. C. Grandjean, A. Boutonnier, C. Guerreiro, J. M. Fournier, L. A. Muard, *J. Org. Chem.* **2005,** *70*, 7123.
S4. E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien and C. B. Murray, *Nature* **2006**, *439*, 55.
S5. J. Park, K. An, Y. Hwang, J. Park, H. Noh, J. Kim, J. Park, N. Hwang, T. Hyeon *Nat. Mater.* **2004,** *3*, 891.
S6. D. Battaglia, B. Blackman, X. Peng, *J. Am. Chem. Soc.* **2005**, *127*, 10889.
S7. Y. Cao, U. Banin, *J. Am. Chem. Soc.* **2000**, *122*, 9692.