Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

of

Stable functionalized PEGylated Quantum Dots Micelles with a controlled stoichiometry

Marian Amela-Cortes,[a] *Victor Roullier,*[a] *Cécile Wolpert,*[a] *Stefanie Neubauer,*[b] *Horst Kessler,*[b] *Olivier Bedel,*[c] *Serge Mignani,*[c] *Valérie Marchi-Artzner*[a]*

[a] Sciences Chimiques de Rennes, Université Rennes 1, UMR 6226 C.N.R.S., Rennes, France.

[b] Institute for Advanced Study and Center of Integrated Protein Science at Technische Universität München, Garching, Germany.

[c] Sanofi-Aventis Recherche et Développement, Centre de Recherche de Vitry-Alforville, 13 Quai Jules Guesde, 94400 Vitry-sur-Seine, France.

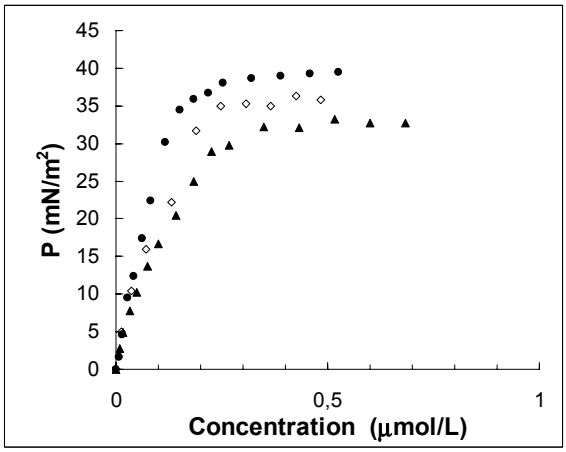


Figure S**1**. Surface pressure for the Langmuir films formed from respectively the ligands **7** (diamond), **9** (dot) and **10** (triangle) on a pure water subphase.

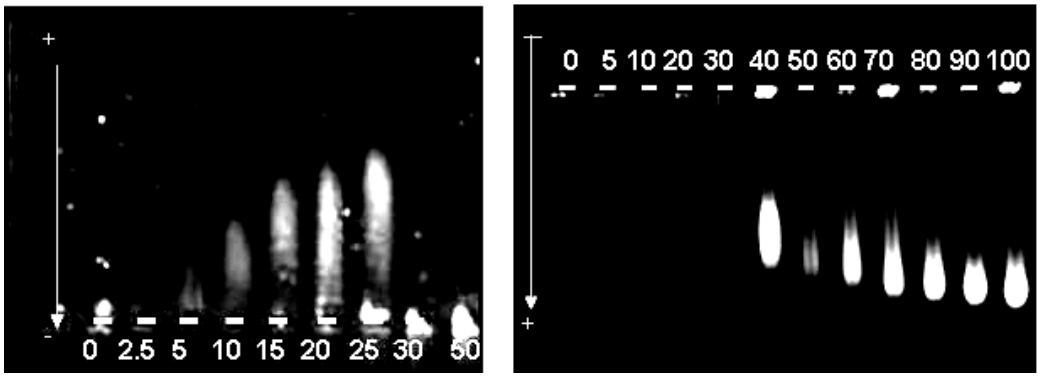
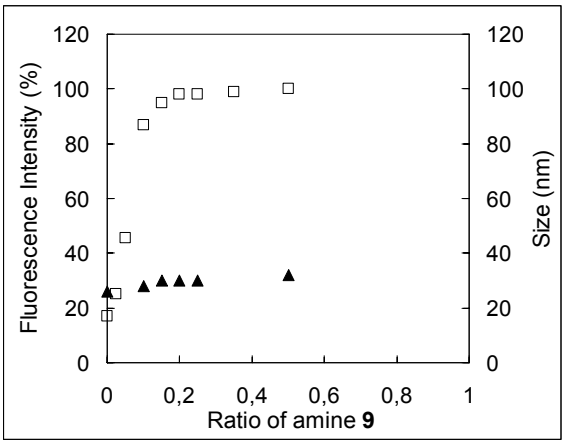


Figure **S2**. Fluorescence Images of the agarose gel electrophoresis corresponding to QD micelles composed of a mixture of **7** and an increasing ratio of charged amphiphiles (% mol): at righ) amine **9** in phosphate buffer pH =5.5, at left) acid **10** in TAE buffer pH = 8.5.

a)



b)

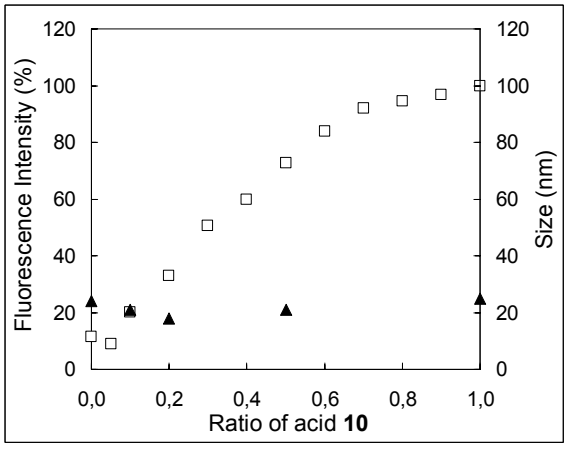


Figure S**3**. Evolution of the normalized emission fluorescence intensity (□) and the mean hydrodynamic diameter (▲) of the **9**/**7** and **10**/**7** QD micelle samples with an increasing molar ratio (%) of: a) amine **9** and b) acid **10**.

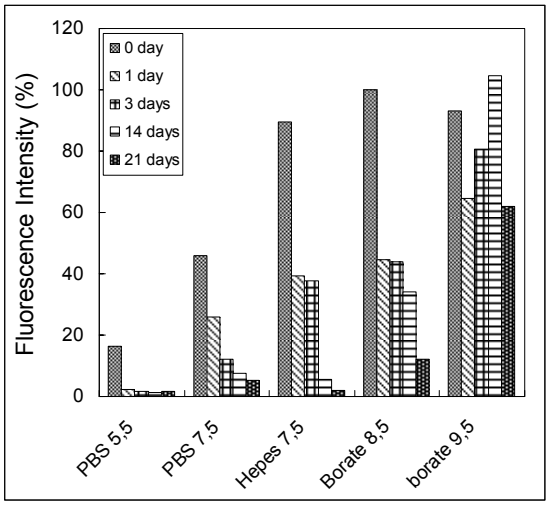


Figure **S4**: Photostability of a solution of polymer Qdot ITK^{TM} carboxyl (Invitrogen) versus pH in different buffers over a period of 21 days.

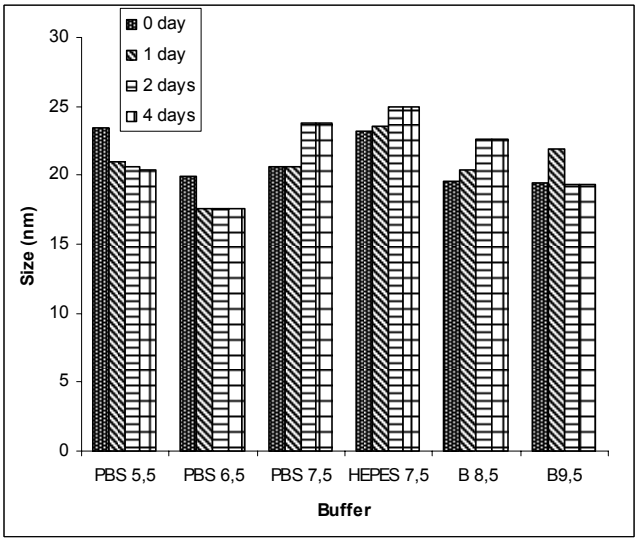
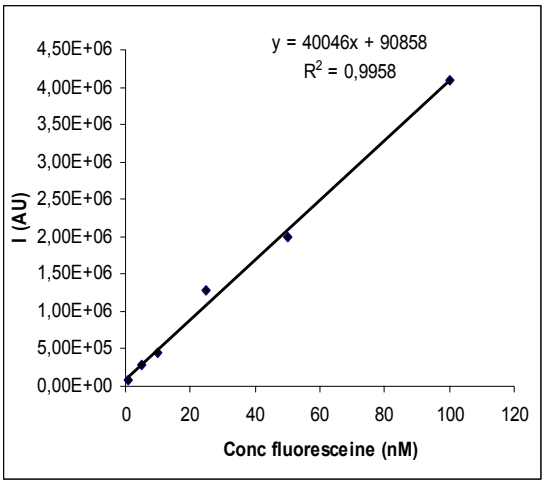


Figure **S5**. Colloidal stability of the **9**/**7** (10/90) QD micelles versus pH over a period of several days estimated by Dynamic Light Scattering.

a)



b)

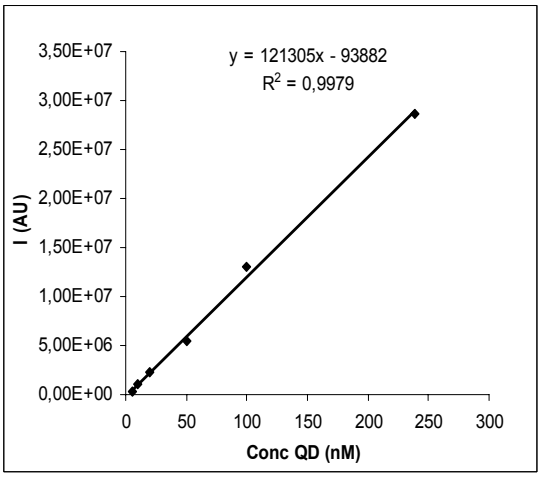
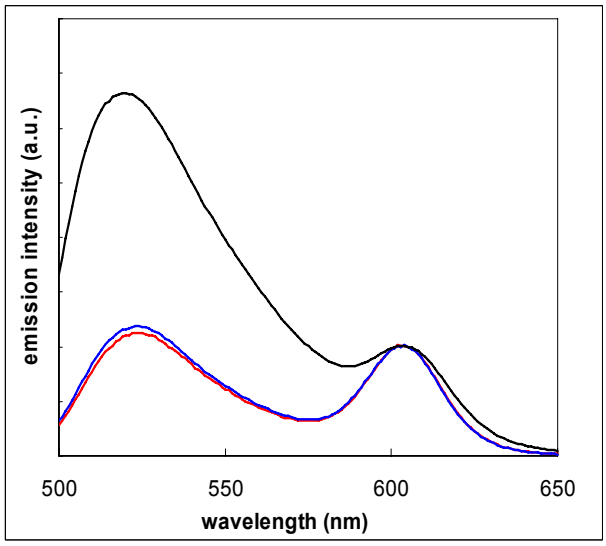


Figure **S6**. Fluorescence calibration curves of a solution containing various concentrations of: **a**) fluorescein, **b**) (**10**/**7**) QD micelles.



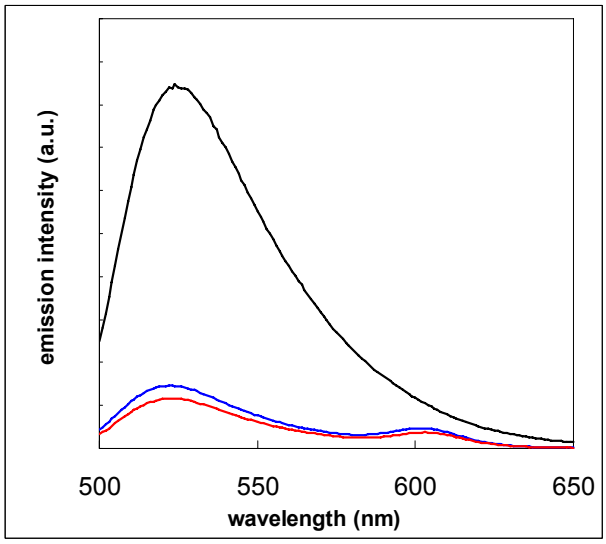


Figure S**7**: Emission intensity spectra of a solution of (**10**/**7**) acid QD after incubation in presence of the coupling agents and fluorescein cadaverin (5-FAM) at two different concentrations: 10 eq (left) or 25 eq (right) of 5-FAM. Corresponding emission intensity spectra before (black F_A^{before}) and after (blue F_A^{after}) elimination of the free fluorescein and of a control solution of fluorescein at the same concentration (red $F_A^{control}$) showing that the emission intensity of cadaverin is almost not quenched by the grafting on QD surface.

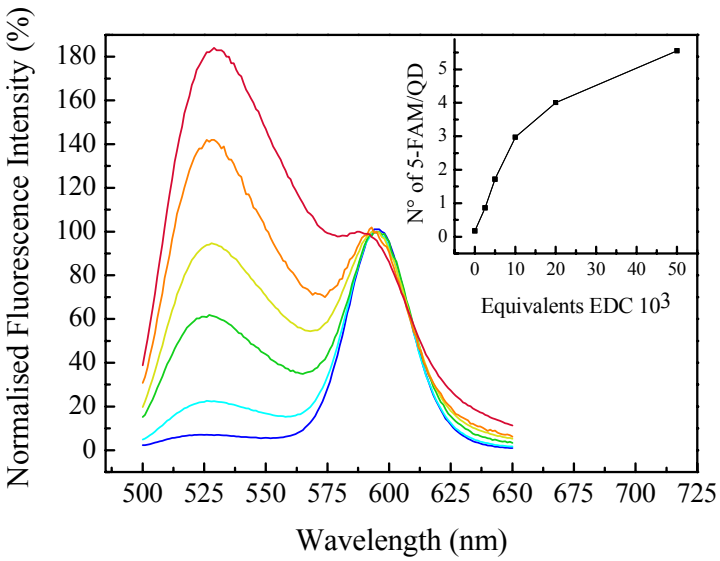


Figure **S8 a**. Evolution of the emission fluorescence intensity spectra during the conjugation of the **10**/**7** (50/50) acid QD to the fluorescein amine by in situ amidation. The molar ratio of QD/fluorescein amine/sulfo-NHS was fixed to (1/250/2500) while the molar ratio of EDC was increased as follows: 0 (blue), 2500 (clear blue), 5000 (green), 10000 (yellow), 20000 (orange), 50000 (red). Insert: mean number of grafted fluroescein per QD versus the number of EDC equivalents (*10^3).

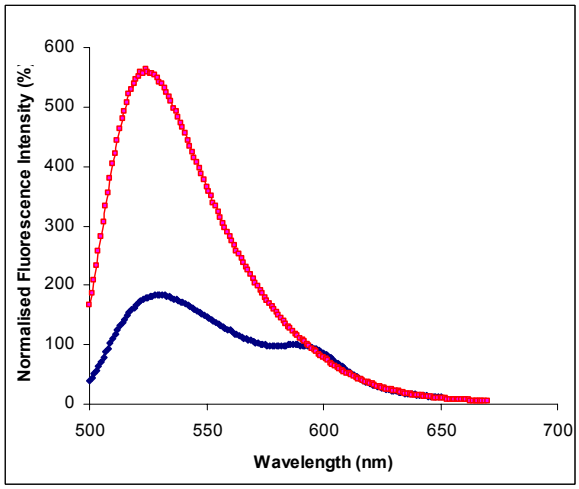


Figure **S8 b**. Evolution of the emission fluorescence intensity spectra during the coupling of **10**/**7** (50/50) acid QD to fluorescein cadaverin (5-FAM) by *in situ* amidation. The molar ratio of QD/fluorescein/EDC (1/250/50000) was fixed while the sulfo-NHS ratio was increased as follows: 2500

(blue), 150000 (red).

Experimental section

Materials and Analysis

All chemicals were purchased from Sigma Aldrich unless indicated and used as received. Hexadecylamine (HDA, 95%) and 1-Tetradecylphosphonic acid (TDPA) were purchased from Alfa-Aesar. 1-Hydroxybenzotriazole hydrate (HOBt), methyl gallate ester and succinic anhydride were purchased from Fluka. Dry solvents were purchased from Sigma Aldrich. All reactions were followed by TLC plates that were visualised with a UV-lamp at 254 nm and revealed with iodine. All the NMR Spectra were performed on a Bruker 300 MHz apparatus.

Cyclic peptide synthesis

The protected peptide (-R(Pbf)GD(*t*Bu)fK(Bzl)-) was synthesized according to SPPS standard Fmoc-procedure[1, 2] using TCP-resign. The compound was cleaved from the resin, cyclized and hydrogenated to yield *cyclo*(-R(Pbf)GD(*t*Bu)fK-).

Synthesis of the PEG gallate amide ligands

Synthesis of α-hydroxyl-ω-tosyl PEG **2**. Poly(ethylenglycol) (average MW 1500) (5 g, 3.3 mmol, 1 eq), Ag_2O (0,924 g, 4 mmol, 1.2 eq) and KI (0.055 g, 0.33 mmol, 0.1 eq) in dichloromethane were placed in a 50-mL round-bottom flask and cooled to 0°C. Tosyl chloride (0.762 g, 4 mmol, 1.2 eq) was added to the solution and the mixture was stirred for 5 hours at 0°C. The precipitated silver salts were then removed by filtration through Celite (Celite®500 fine Sigma Aldrich) which was washed thoroughly with dichloromethane. The combined filtrate was concentrated and the residue was purified on silica gel with 1:0 to 9:1 CH_2Cl_2 : MeOH as the eluent yielding 1,37g (36.7 %) of a waxy white powder.^{1}H-NMR (300 MHz, $CDCl_3$): δ7.85 (d, 2H, J = 8.31 Hz), 7.40 (d, 2H, J = 7.9 Hz), 4.20 (t, 3H, J = 4.9 Hz), 3.80-3.60 (m, 134H), 2.50 (s, 3H, -CH_3)

Synthesis of α-Azide-ω-hydroxyl PEG **3**.

2 (1,37 g, 0,83 mmol, 1 eq) was dissolved in DMF (20 mL), followed by sodium azide (52 mg, 1.24 mmol, 1.5 eq) addition and stirred overnight at 110°C. After solvent evaporation and suspension in dichloromethane, the white salts were filtered off and the filtrate was concentrated to yield 1.187 g (84.5%) of the compound **3**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.80-3.60 (m), 3.40 (t, 2H, J = 5.28 Hz).

Synthesis of α-Azide-ω-tosyl PEG **4**.

To a solution of **3** (1.54 g, 1.01 mmol, 1 eq) in dry dichloromethane (50 mL) were added Ag_2O (0.47 g, 2.02 mmol, 2 eq), KI (67.3 mg, 0.4 mmol, 0.4 eq) and tosyl chloride (0.396 g, 2.02 mmol, 2 eq). After stirring the solution at reflux overnight, the silver salts were filtrated through Celite®. The filtrate was then concentrated and the residue was chromatographied on silica gel with (1:0 to 9:1) CH_2Cl_2: MeOH mixture as eluent. Yield 1.28 g, 75.4%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ7.85 (d, 2H, J = 8.31 Hz), 7.40 (d, 2H, J = 7.9 Hz), 4.20 (t, 3H, J = 4.9 Hz), 3.80-3.60 (m, 134H), 3.40 (t, 2H, J = 5.28 Hz), 2.50 (s, 3H)

Synthesis of the 3,4,5 undecanoxy gallate acid ***5***. Methyl gallate (2 g, 10 mmol, 1 eq), and potassium carbonate (13.8 g, 100 mmol, 10 eq) were loaded into a 250 mL round-bottom flask and dissolved in 50 mL of dry DMF. To that 1-bromoundecane (8.4 g, 36 mmol, 3.6 eq) were added and the reaction heated for four days at 80°C. When the reaction was finished, 100 mL of cold water were poured into the flask and the organic phase was extracted with dichloromethane (3 x 40 mL) and washed with brine (3 x 20 mL). The organic layer was then recombined and dried over anhydrous magnesium sulphate and the solvent evaporated. The tri-substituted methyl ester (6.535 g, 93%) was obtained as an oil.^{1}H-NMR (300 MHz, $CDCl_3$): δ7.33 (s, 2H), 4.0 (tt, 6H, J = 6.7 Hz, J = 6.4 Hz), 3.9 ppm (s, 3H), 1.84 (m, 6H), 1.49-1.28 (cs, 49H), 0.90 (t, 9H, J = 6.7 Hz).

The obtained tri-substituted methyl ester (6.3 g, 9.7 mmol, 1 eq), was refluxed in a NaOH (4 g, 100 mmol, 10 eq) ethanol (50mL) mixture for six hours. Afterwards the ethanol was evaporated and the precipitate dissolved in 20 mL of deionised water. The solution was then neutralized with concentrated

hydrochloric acid. The aqueous layer was extracted with ethylacetate (3 x 15 mL) and the organic layer was dried over anhydrous magnesium sulphate and the solvent evaporated. The solid obtained was crystallised from ethanol, giving rise to 5.725 g (90%) of the compound **5**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ7.33 (s, 2H), 4.06 (tt, 6H, J = 6.7 Hz, J = 6.4 Hz), 1.84 (m, 6H), 1.49-1.28 (sc, 49H), 0.90 (t, 9H, J = 6.7 Hz).

*Synthesis of Gallate-PEG-tosyl **6**.* The azide PEG **4** (1.28 g, 0.76 mmol, 1 eq) was dissolved in 2 mL of toluene and to that a solution of triphenylphosphine (0.4 g, 1.5 mmol, 2 eq) in 1 mL of toluene was added. The reaction was stirred at room temperature overnight. In another flask, **5** (0.967 g, 1.5 mmol, 2 eq), dimethylaminopyridine (0.139 g, 1.14 mmol, 1.5 eq) and 1-hydroxybenzotriazol (HOBt) (0.229 g, 1.5 mmol, 2 eq) were dissolved in dioxane (5 mL) and the mixture was degasified for 1 hour. Afterwards, EDC (0.29 g, 1.5 mmol, 2 eq) was added and the solution stirred at room temperature for 10 minutes. Then, the iminophosphorane stock solution was added dropwise to the reaction mixture and the reaction was maintained under stirring at room temperature for 24 hours. After evaporation of the solvent, the mixture was purified by silica gel column chromatography with 1:0 to 9:1 CH_2Cl_2: MeOH as the eluent. 346 mg (64 %) of **6** as a waxy solid were isolated.^{1}H-NMR (300 MHz, $CDCl_3$): δ7.80 (d, 2H, J = 8.3 Hz), 7.35 (d, 2H, J = 8.3 Hz), 7.01 (s, 2H), 6.75 (t, 1H), 4.17 (t, 2H, J = 4.5 Hz), 3.99 (tt, 6H, J = 6.4 Hz, J = 13.1 Hz) 3.80-3.60 (m, 134H), 2.50 (s, 3H), 1.81 (m, 6H) 1.6-1.3 (sc, 49H), 0.89 (t, 3H, J = 6.4 Hz).

Synthesis of Gallate-PEG-OH 7.

In a round-bottom flask equipped with a refrigerant, **6** (488 mg, 0.215 mmol, 1eq) was dissolved in dry methanol (5 mL) followed by the addition of magnesium turnings (69.7 mg, 2.86 mmol, 13 eq). The reaction was left stirring under argon overnight at room temperature. When the reaction was finished, crude was neutralised with chilled 5 % hydrochloric acid and then the product was extracted against dichloromethane (6 x 60 mL). The solvent was then evaporated yielding 375 mg (82.5 %) of a yellow-

orange waxy solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.9 (t, 1H), 3.99 (tt, 6H, J = 6.4 Hz, J = 12.8 Hz) 3.80-3.60 (m, 134H), 1.81 (m, 6H) 1.5-1.2 (sc, 49H), 0.89 (t, 3H, J = 6.4 Hz).

Synthesis of Gallate-PEG-N_3 ***8***.

6 (500 mg, 0.22 mmol, 1 eq) and sodium azide (21.5 mg, 0.33 mmol, 1.5 eq) were dissolved in dry DMF (10 mL) and the reaction was kept under argon at 80°C overnight. The DMF was then removed under reduced pressure and 411.7 mg (88.3%) of a waxy white solid were obtained.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.9 (t, 1H), 3.99 (tt, 6H, J = 6.4 Hz, J = 13.0 Hz) 3.80-3.60 (m, 134H), 3.42 (t, 2H, J = 5.2 Hz), 1.81 (m, 6H) 1.5-1.2 (sc, 49H), 0.89 (t, 3H, J = 6.4 Hz).

Synthesis of Gallate-PEG-NH_2 ***9***.

8 (411.7 mg, 0.192 mmol, 1eq) was hydrogenated in presence of Pd/C (10 % in mass). The reaction was stirred under hydrogen at room temperature overnight. The Pd/C was filtered off through Celite and washed with dichloromethane. After evaporation of the solvent, 400 mg (Yield = 99%) of the product **9** were obtained.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.9 (t, 1H), 3.99 (tt, 6H, J = 6.4 Hz, J = 13.0 Hz) 3.88 (t, 3H), 3.80-3.60 (m, 134H), 3.2 (t, 2H), 1.81 (m, 6H) 1.5-1.2 (sc, 49H), 0.89 (t, 3H, J = 6.4 Hz).

Synthesis of Gallate-PEG-acid ***10***.

9 (300 mg, 0.142 mmol, 1 eq), dimethylaminopyridine (65.3 mg, 0.426 mmol, 3 eq) and succinic anhydride (43.1 mg, 0.426 mmol, 3 eq) were mixed and dried under vacuum for one hour. Afterwards, triethylamine (42.9 mg, 0.426 mmol, 3 eq) was added and the mixture was dissolved in dichloromethane anhydrous. The reaction was stirred under argon overnight. The crude was then successively washed with hydrochloric acid at pH 3 (3x 60 mL), water (3 x 60 mL) and finally brine (3 x 60 mL). The organic layer was dried over magnesium sulphate and the solvent evaporated. 224 mg (72.3 %) of the product were isolated.^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.9 (t, 1H), 4.01 (tt, 6H, J = 6.4 Hz, J = 10.0 Hz), 3.80-3.60 (m, 134H), 2.64 (t, 2H, J = 7.4 Hz), 2.56 (t, 2H, J = 7.5 Hz) 1.81 (m, 6H) 1.5-

1.2 (sc, 49H), 0.89 (t, 3H, *J* = 6.4 Hz).

*Synthesis of Gallate-PEG-RGD **11**.*

10 (50 mg, 0.0229 mmol, 1 eq), HATU (8.45 mg, 0.022 mmol, 0.97 eq) and diisopropylethylamine (27.75 mg, 0.229 mmol, 10 eq) were dissolved in dry DMF (1 mL) to pH 8.5-9. The used cyclic c(R(Pbf)GD(tBu)fK) peptide was prepared according the procedure previously described.[3] To that a solution of the cyclic protected peptide (1 eq, 0.25 mL in anhydrous DMF) was added. The reaction was kept at room temperature overnight. The solvent was then removed under pressure and the product isolated by column chromatography with 1:0 to 9:1 CH_2Cl_2: MeOH as the eluent. The peptide gallate amide was then deprotected with TFA to provide **11**. This compound was characterized by HPLC performed on a column (acquity BEH300C4 Waters 1.7 uM, 2.1*150 mm) with a H_20 gradient + 0.1 % HCO_2H/CAN + 0.1 % HCO_2H during 10 min. Corresponding Mass Spectrum performed by coupled Xevo QTOF Mass spectroscopy used in electrospray positive mode. Calculated Mass of **11**: 2813.7874, found 2813.7.

Synthesis of CdSe/ZnS and CdTe/CdSe quantum dots

CdSe/ZnS QD have been synthesised following the two steps synthesis described previously in the literature.[4, 5] Core synthesis: CdO (0.0514 g, 0.4 mmol), TOPO (3.17114 g, 9.6 mmol), HDA (1.928 g, 8 mmol), TDPA (0.245 g, 0.88 mmol) were mixed and heated three-necked round-bottom flask at 320°C under Schlenk conditions. After complete decolouration, the mixture was cooled down to 270°C. Meanwhile a 90% Selenium stock solution was prepared using Selenium (0.315 g, 4 mmol), in TOP (8 mL) and was injected rapidly into the reaction mixture at 270°C. The reaction was stopped by cooling the reaction vessel to 65°C, when the desired emission wavelength was reached (2 min, 590 nm). The CdSe cores were purified by precipitation in methanol / chloroform and dispersed in pentane. For the shell synthesis TOPO (3.711 g, 7.2 mmol), HDA (1.928 g, 8 mmol) were stirred for 1 hour at 150 °C under vacuum. After cooling down the mixture to 60°C, the pentane core solution was added and the

pentane removed under vacuum. The reaction mixture was heated up at 160 °C under argon flow. The shell precursor solution was prepared by mixing TOP (2 mL), diethylzinc (265 µL, 1M in pentane) and $(TMS)_2S$ (72 µL) and injected into the core flask at a rate of 2 mL/h. The optical properties were followed by UV-spectroscopy and fluorimetry. After cooling to room temperature the concentration of the resulting CdSe/ZnS QD solution was estimated from the optical density of the solution at 350 nm.

Synthesis and characterization of the QD micelles

QD Solubilization into water. A mixture of appropriated amount of amphiphilic ligands and hydrophobic CdSe/ZnS QD were dispersed in chloroform prior drying under a reduced pressure (300 mBar). The QD micelles were obtained afterwards by hydration of the mixture in aqueous solution at 50°C for 60 minutes. The suspension was then centrifuged at 20000 g for 10 minutes to remove aggregates. The ligand excess was eliminated by passing the QD micelles through a NAP-5 disposable desalting column (Sephadex, GE Healthcare).

Optical spectroscopic measurements. The absorbance was recorded by Cary 100 UV-visible spectrophotometer (Varian, Australia).

Fluorescence measurements. Fluorescence properties of QD micelles were investigated with a Fluorolog-3 fluorescence spectrometer (FL3-22, Horiba Jobin Yvon). Fluorescence Quantum Yield of amphiphile QD micelles was measured in comparison to Rhodamine 6G (Molecular Probes Invitrogen) in ethanol used as a reference.

Dynamic Light Scattering. The scattered intensity was collected at a 173° angle on a Zetasizer Nano-ZS (Malvern Instruments, England) apparatus at 25°C. All samples were filtrated through 0.2 µm Millipore filter (Millex GV, Sigma-Aldrich, France).

Agarose Gel Electrophoresis. Electrophoresis migrations of QD micelles were performed by using a GEL XL ULTRA V-2 device (Labnet International corporation) and a 0.5% agarose gel in either PBS (10 mM, pH 5.5) or TAE (10 mM Tris-acetate, 0.4 mM EDTA, pH = 8.5) under a 50 V electric field for

1 hour.

Critical Micellar Concentration (CMC) estimation. Surface pressures were measured by the Wilhelmy plate and a pressure sensor type PS4 (NIMA technology, Coventry, England). Aliquots of a chloroform solution of the appropriated amphiphile (**7**, **9** or **10**) at 50 μM concentration were added to a teflon cell containing pure water (Millipore). The system was let to equilibrate after each measurement and the measured surface pressure was plotted against the amphiphile concentration.

QD Stability versus the pH. The photostability of the QD was measured in the case of amine **9**/**7** (10 / 90) QD, acid **10**/**7** (50 / 50) QD and commercial polymer Qdot ITK^{TM} carboxyl (Invitrogen). The solutions were incubated in PBS buffer ranging from 5.5 to 7.5, Hepes 7.5 and borate buffer ranging from 8.5 to 9.5 at room temperature in the dark at 70 nM. Fluorescence intensity was measured at different time laps (until 1 month) with excitation at 350 nm.

Covalent coupling of acid QD micelles to fluorescein. Acid **10**/**7** (50/50) QD were covalently coupled to the fluorescein amine (Cadaverine 5-FAM purchased from Molecular Probes) via EDC and sulfo-NHS coupling agents. Solution of acid QD 1 μM in PBS (phosphate buffer, 100 mM, 150 mM NaCl, pH = 7.5) was incubated with 2500 equivalents of sulfo-NHS for 10 minutes under stirring. To that, a solution of EDC in PBS was added with concentrations ranging from 0 to 50000 equivalents and the carboxylic acids were let to activate for 15 minutes. A solution of 5-FAM with concentrations ranging from 0 to 1000 equivalents was then added and the reaction was kept under stirring for three hours at room temperature. The conjugated fluorescein-QD dispersion was purified via successive centrifugations in borate buffer (20 mM, 150 mM NaCl, pH 8.5) using Vivaspin 500 (10000 MWCO, Polyethersulfone, Sartorius). Final purification through NAP 5 column in borate buffer allowed to separate bound from unbound fluorescein amine. Fluorescence spectra of the solutions were recorded to determine the efficiency of the coupling reaction with an excitation wavelength at 492 nm corresponding to the absorption maximum of the fluorescein. Control samples were carried out without EDC and sulfo-NHS

coupling agents followed by the same purification as for conjugated fluorescein-QD.

Calculation of the mean number of grafted fluorescein (5-FAM) per QD. After incubation in presence of the activation agents, the emission intensity of fluorescein *(*noted *A)* can be written as a sum of the contributions of the free (F_A^{free}) and the grafted fluorophores *A* on the QD (F_A^{QD}) for each mixture of (**10**/**7**) acid QD and fluorescein cadaverin *A*. At the end of the coupling reaction, the emission intensities of *A* (corresponding to its maximum of absorption) were recorded before and after elimination of free *A* by size exclusion gel chromatography. These intensities (respectively F_A^{before} and F_A^{after}) can be written as follows:

$$F_A^{before} = x \, .F_A^{QD} + (1-x). \, F_A^{free}$$

$$F_A^{after} = x \, .F_A^{QD}$$

where x is the ratio of *A* grafted to QD surface.

then $F_A^{before} - F_A^{after} = (1-x) \, F_A^{free}$ and $x= 1 – (F_A^{before} - F_A^{after})/F_A^{free}$

The concentration of *A* (after elimination of free A) was calculated from the calibration curve. As a control, the emission intensity of a solution of free *A* at the same concentration ($F_A^{control}$) was recorded and then compared to F_A^{after}. The emission intensity spectra, obtained for two different initial concentrations of *A*, are shown in Figure **S6**. This control experiment demonstrates that the quenching of the bound fluorescein (grafted *A*) is very low on the QD surface.

FRET between covalently linked amine QD and CY5-NHS. Solutions of amine **9**/**7** (10/90) QD (35 nM) in borate buffer (20 mM, 150 NaCl, pH 8.5) were mixed with different amounts of a solution of Cy5-NHS (Molecular Probes) in DMSO (1 mM, from 0 to 100 equivalents). The FRET response of the conjugated CY5-QD was characterised by fluorescence measurements with an excitation wavelength at 420 nm. All the emission spectra were corrected from the direct excitation of the CY5 by substrating the corresponding emission spectra of Cy5-NHS with the same concentration and excitation wavelength.

High-Pressure Liquid Chromatography (HPLC). Analysis of QD alone and covalently coupled QD-CY5 conjugates were carried out on an AKTÄ-purifier-10 HPLC system monitored by Unicorn Manager 5.1 software. The fluorescence was monitored by a Shimadzu fluorescence detector (RF-10AXL). The 597 nm emitting QD were excited at 350 nm whereas the 690 nm emitting CY5-QD conjugates nm were excitated at 440 nm. A Superdex 200 (3.2 x 300 mm, 13 μm, Amersham Biosciences, France) was used with phosphate buffer saline mobile phase (100 mM phosphate buffer, 150 mM NaCl, pH 7.4) at a flow rate of 0.04 mL/min.

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