

Electronic Supplementary Information

Tunable hydroxylated surfactants – An efficient toolbox towards anisotropic gold nanoparticles

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1- Supplementary methods

1.1- General

Tetrachloroauric acid hydrate, $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ (99.9%), sodium borohydride, (+)-*L*-ascorbic acid (99%), CTAB and silver nitrate - AgNO_3 (99%) were used as purchased. The HAAX surfactants were synthesized by a procedure already described.²⁸⁻³⁰ Distilled water was used to prepare all solutions. Absorption spectra of the solutions were carried out on a Shimadzu UV-vis-NIR 1800 spectrophotometer, using optical glass cells with length of 1cm. TEM analyses were recorded on a transmission electron microscope (JEOL, JEM 100CX II UHR) at an accelerating voltage of 100 kV.

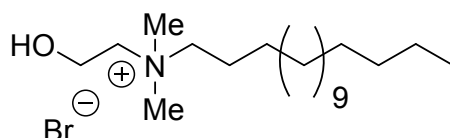
1.2- Hydroxylated surfactant synthesis

Bromododecane, Bromohexadecane, Bromooctadecane and all halogenated derivatives, (*N,N*-dimethylamino)-1-alcohol, *N,N*-dimethylhexadecylamine were purchased from Aldrich or Fluka and were used without further purification. The surfactants were prepared as described in the literature or after adapted modification, and characterized. NMR spectra were recorded using a BRUCKER Avance III 400 spectrometer at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C . All magnetic resonance spectra were quoted in parts per million (ppm) measured from tetramethylsilane (TMS) as external reference. The following abbreviations were used to describe peak splitting patterns when appropriate: s= singlet, t= triplet, m= multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). All melting points were measured using a Stuart melting point apparatus SMP3. The sample was added in a capillary tube that was accommodated in a heating block. Then, the melting process was observed with the help of bright illumination and a powerful magnifying glass. The CMC measurements were performed using an automatic tensiometer (Krüss K100) and the DuNoüy Ring Method for air-water interface at 298 K. Before each experiment, the platinum ring was cleaned in a water/ethanol mixture and then in a blue color flame. A concentrated solution 1mg/mL (5 mL) was put in a conic vessel (165.7 mL) and was reduced by the addition of small amounts of ultrapure water. After each addition, the solution is stirred for 120 s. The immersion depth of the ring is 1 mm. Equilibrium surface tension was measured three times at 25°C for each concentration with Harkins and Jordan correction method.

1.2.1. *N,N*- dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium bromide salt HEA16Br

In a 25mL-flask, 10.7 mL (35.1 mmol, 1.2 eq.) of 1-bromohexadecane and 3,0 mL (29.2 mmol, 1 eq.) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

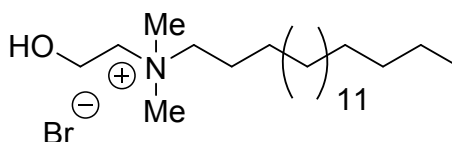
White powder, 92% yield, C₂₀H₄₄BrNO (394.47 g.mol⁻¹), CMC = 0.77 mmol.L⁻¹, m.p. 207-208°C, ¹H NMR (400MHz, CDCl₃, 25°C, TMS): δ = 0.85 (t, *J* = 7 Hz, 3H), 1.23 (m, 24H), 1.32 (m, 2H), 1.73 (m, 2H), 3.36 (s, 6H), 3.56 (m, 2H), 3.74 (m, 2H); 4.10 (m, 2H); 5.0 (t, *J* = 5.3 Hz, 1H). ¹³C NMR (400MHz, CDCl₃, 25°C, TMS): δ = 14.1, 22.6- 31.9, 52.1, 55.8, 65.6, 66.0 ppm.



1.2.2. *N,N*- dimethyl-*N*-octadecyl-*N*-(2-hydroxybutyl)ammonium bromide salt HEA18Br

In a 25mL-flask, 11.98 mL(35.1 mmol, 1.2 eq, 11.7 g) of 1-bromooctadecane and 3.0 mL (29.2 mmol, 1 eq., 2.6g) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

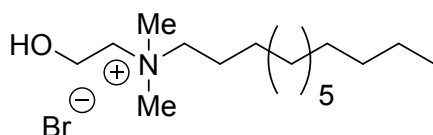
White powder, 95% yield, C₂₂H₄₈BrNO (421.29 g.mol⁻¹), CMC = 0.19 mmol.L⁻¹, m.p. 208-210°C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 0.86 (t, *J* = 7 Hz, 3H), 1.23 (m, 28H), 1.33 (m, 2H), 1.73 (m, 2H), 3.24 (m, 2H), 3.30 (s, 6H), 3.54 (m, 2H); 3.97 (m, 2H); 5.0 (t, *J* = 5.3 Hz, 1H). ¹³C NMR (400MHz, CDCl₃, 25°C, TMS): δ = 14.1, 22.8 - 31.9, 52.5, 64.8, 65.0, 67.7 ppm.



1.2.3. *N,N*- dimethyl-*N*-dodecyl-*N*-(hydroxyethyl)ammonium bromide salt HEA12Br

In a 25mL-flask, 8.8 mL (35.1 mmol, 1.2 eq, 8.75 g) of 1-bromododecane and 3.0 mL (29.2 mmol, 1 eq., 2.6g) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

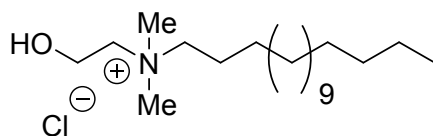
White powder, 95% yield, C₁₆H₃₆BrNO (337.2 g.mol⁻¹), CMC = 2.1 mmol.L⁻¹, m.p. 202-204°C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 0.86 (t, *J* = 7 Hz, 3H), 1.29 (m, 20H), 1.33 (m, 2H), 1.73 (m, 2H), 3.26 (m, 2H), 3.31 (s, 6H), 3.43 (m, 2H); 3.97 (m, 2H); 5.0 (t, *J* = 5.3 Hz, 1H). ¹³C NMR (400MHz, CDCl₃, 25°C, TMS): δ = 14.1, 22.8 - 31.9, 52.5, 64.8, 65.0, 67.7 ppm.



1.2.4. *N,N*- dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt HEA16Cl

In a 25mL-flask, 10.6 mL (35.1 mmol, 1.2 eq, 9.16 g) of 1-chlorohexadecane and 3.0 mL (29.2 mmol, 1 eq., 2.6g) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 48h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

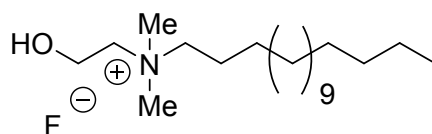
White powder, 92% yield, C₂₀H₄₄ClNO (350 g.mol⁻¹), CMC = 0.19 mmol.L⁻¹, m.p. 204 °C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=0.81 (t, *J*=7.1 Hz, 3H), 1.18 (m, 24H), 1.27 (m, 2H), 1.67 (m, 2H), 3.30 (s, 6H), 3.48 (m, 2H), 3.48 (m, 2H), 3.65 (m, 2H), 4.03 (m, 2H), 4.61 (m, 1H) ppm. RMN-C¹³ (CDCl₃): δ= 14.09, 22.7 – 31.09, 52.0, 55.9, 65.7, 66.0 ppm. RMN-H¹ (D₂O): δ= 0.80 (t, *J*= 6.8 Hz, 3H), 1.21-1.28 (m, 2H), 1.70 (m, 2H), 3.09 (s, 6H), 3.34 (m,2H), 3.44 (m, 2H), 3.94 (m, 2H) ppm. ¹³C RMN: δ= 13.87, 22.45-32.03, 51.55, 55.41, 65.04, 65.7, 66 ppm.



1.2.5. *N,N*- dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium fluoride salt HEA16F

In a 25mL-flask, 2g of HEA16Cl (1 eq., 5.7 mmol) and 0.37g of KF (1.1 eq., 6.3 mmol) were added in acetone or methyl alcohol (40 mL) and the reaction mixture was stirred under reflux for 48h. After the reaction, the system is filtered through celite and the solvent removed. The solid is washed twice with diethyl ether and filtered.

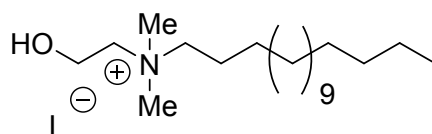
White powder, 97% yield, C₂₀H₄₄ClNO (333.5 g.mol⁻¹), CMC = 2.12 mmol.L⁻¹, m.p. 75-80 °C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ= 0.81 (t, *J*=7.1 Hz, 3H), 1.18 (m, 24H), 1.27 (m, 2H), 1.67 (m, 2H), 3.30 (s, 6H), 3.48 (m, 2H), 3.48 (m, 2H), 3.65 (m, 2H), 4.03 (m, 2H), 4.61 (m, 1H) ppm. C¹³-RMN (CDCl₃): δ= 14.09, 22.7 – 31.09, 52.0, 55.9, 65.7, 66.0 ppm. F¹⁹ RMN (CDCl₃): δ= -146.53. RMN-H¹ (D₂O): δ= 0.72 (t, *J*=6.8 Hz, 3H), 1.15-1.21 (m, 27H), 1.62 (m, 2H), 3.0 (s, 6H), 3.20 (m, 2H), 3.34 (m, 2H), 3.86 (m, 2H) ppm. RMN-C¹³ (D₂O): δ= 13.85, 22.35-31.97, 51.48, 55.35, 65.06 ppm. RMN F¹⁹ (D₂O): δ= -122.23 ppm.



1.2.6. *N,N*- dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium iodide salt HEA16I

In a 25mL-flask, 11 mL (35.1 mmol, 1.2 eq, 12.36 g) of 1-iodohexadecane and 3.0 mL (29.2 mmol, 1 eq., 2.6g) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

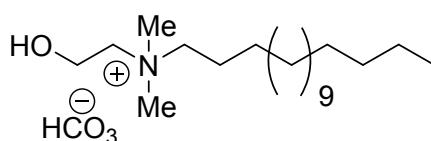
Light yellow powder, 84% yield, C₂₀H₄₄INO (441.47g.mol⁻¹), CMC = 0.013 mmol.L⁻¹, m.p. 176-178 °C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=0.85 (t, *J*=7.1 Hz, 3H), 1.23 (m, 24H), 1.34 (m, 2H), 1.75 (m, 2H), 3.36 (s, 6H), 3.55 (m, 2H), 3.76 (m, 2H), 4.16 (m, 2H)ppm. RMN-C¹³ (CDCl₃): δ= 14.2, 22.7 – 31.09, 52.5, 55.8, 65.6, 66.4 ppm.



1.2.7. *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium hydrogenocarbonate salt HEA16HCO₃

In a 25mL-flask, 2g of HEA16Cl (1 eq., 5.7 mmol) and 0.53g of NaHCO₃ (1.1 eq., 6.3 mmol) were added in acetone or methyl alcohol (40 mL) and the reaction mixture was stirred under reflux for 48h. After the reaction, the system is filtered through celite and the solvent removed. The solid is washed twice with diethyl ether and filtered.

White powder, 97% yield, C₂₀H₄₄ClNO (375 g.mol⁻¹), CMC = 0.6 mmol.L⁻¹, m.p. 210-215°C, ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ= 0.81 (t, *J*=7.1 Hz, 3H), 1.18 (m, 24H), 1.27 (m, 2H), 1.67 (m, 2H), 3.30 (s, 6H), 3.48 (m, 2H), 3.65 (m, 2H), 4.03 (m, 2H), 4.61 (m, 1H) ppm. C¹³-RMN (CDCl₃): δ= 14.09, 22.7 – 31.09, 52.0, 55.9, 65.7, 66.0 ppm. RMN-H¹ (D₂O): δ= 0.79 (t, *J*=7.1 Hz, 3H), 1.21 (m, 27H), 1.69 (m, 2H), 3.08 (s, 6H), 3.31 (m, 2H), 3.42 (m, 2H), 3.93 (m, 2H) ppm. RMN-C¹³ (D₂O): δ= 13.84, 22.45, 26.24-32.04, 51.54, 55.38, 64.97, 65.10 ppm.



1.3. Gold Nanoparticles synthesis

AuNPs prepared in this study were produced by a seeded-growth method, adapted from the protocols developed by Murphy⁶ and El Sayed.¹⁹ The method consists in preparing two solutions: i) the seed solution and ii) the growth solution.

Seed solution: In a 25 mL-flask, 0.1 mL of an aqueous solution of HAuCl₄.3H₂O (0.025 mol.L⁻¹, 0.0025 mmol) was added to a 7.4 mL aqueous solution of surfactant (0.0676 mol.L⁻¹, 0.5 mmol) (in the case of HEA18Br, a 7.4 mL aqueous solution of surfactant (0.0337 mol.L⁻¹, 0.25 mmol) was used). Then, under stirring, 0.6 mL of an ice-cold aqueous solution of sodium borohydride (0.01 mol.L⁻¹, 0.006 mmol) was added. The solution color immediately turned to brown. After 2 min, the system remains at least 2 h, without stirring before used.

Growth Solution: In a 25 mL-flask, 0.2 mL of an aqueous solution of HAuCl₄.3H₂O (0.025 mol.L⁻¹, 0.005mmol) was added to a 7.3 mL aqueous solution of surfactant (0.0685 mol.L⁻¹, 0.5

mmol) (except for HEA18Br, a 7.3 mL aqueous solution of surfactant (0.0342 mol.L⁻¹, 0.25 mmol) was used). Then, 0.15 mL of an aqueous solution of silver nitrate (4 x 10⁻³ mol.L⁻¹) was added under stirring, followed by ascorbic acid (0.070 mL, 0.0788 M). The system turned to colorless, proving the reduction of Au³⁺ to Au⁺.

Growing process: 0.060 mL of seed particles were added to the freshly prepared growth solution. The solution is kept under stirring for just 10 s and then allowed to stand for 4 h without stirring prior to characterization to ensure the system stability.

2- TEM and UV-Vis/near-IR characterization

Transmission Electron Microscopy images were obtained on a Microscope JEOL TEM 100CXII operating at 100kV. The samples were prepared with a thin film of the gold nanorods solution on a copper grid coated with carbon film at minimum of 24 hours before analysis to dry sufficiently maintained in a dissector. The analyses of UV-Vis/near-IR measurements were carried out on a Shimadzu UV-vis 1800 spectrophotometer. The set-up was configured to fix the baseline of distilled water absorption band from 400 to 1000 nm, using optical glass cells with length of 1cm.

2.1- Gold Nanoparticles produced with CTAB

Pictures obtained from samples prepared with 24 hours. The synthesis and TEM analyses were preliminary described in [RSC Adv. 2013, 3, 18292]

Mean size: 40.8 nm x 12.4 nm (± 4.8 nm x 2.3 nm)

Aspect ratio: 3.3

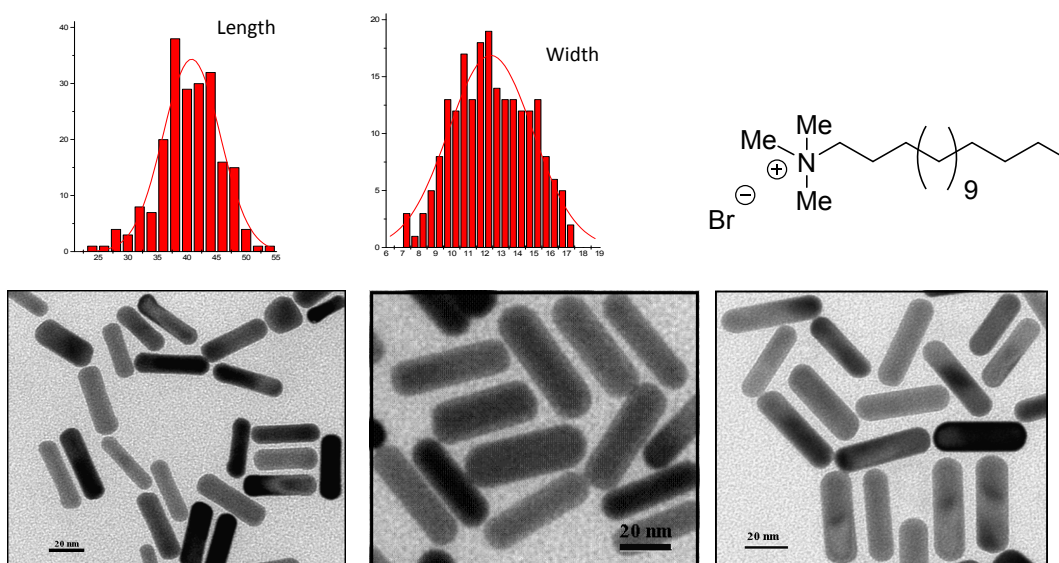


Figure ESI1. TEM images and size distributions of AuNR @ CTAB

2.2 Gold Nanoparticles produced with HEA16Br

Pictures obtained from samples prepared with 24 hours. The synthesis and TEM analyses were preliminary described in [RSC Adv. 2013, 3, 18292]

Mean size: 30 nm x 10 nm (± 5.5 nm x 1.3 nm)

Aspect ratio: 3.0

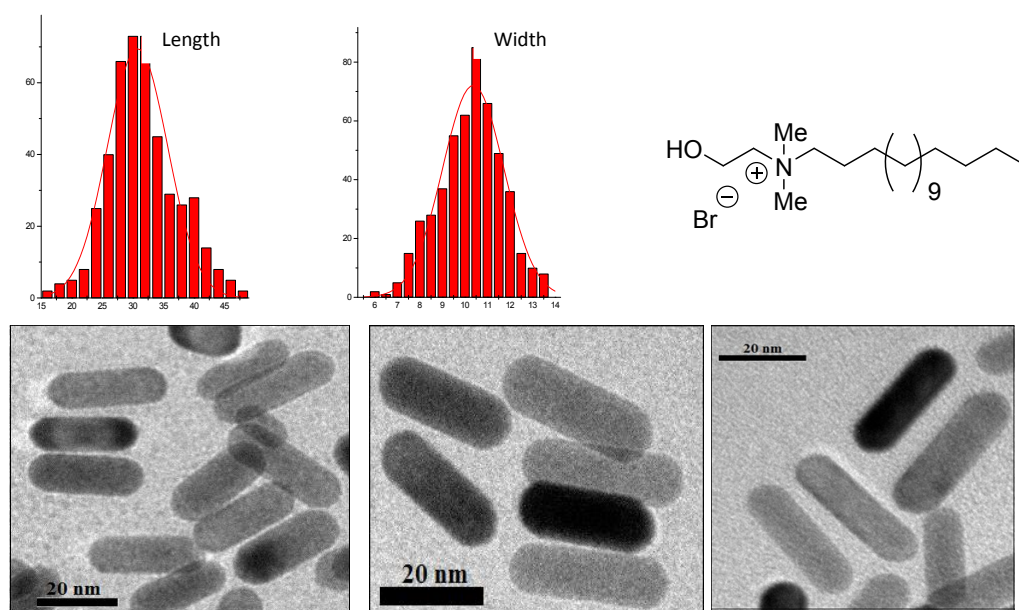


Figure ESI2. TEM images and size distributions of AuNR@HEA16Br

2.3 Gold Nanoparticles produced with HEA18Br

Pictures obtained from samples prepared with 24 hours.

Mean size: 45 nm x 14 nm ($\pm 11,6$ nm x 2.3 nm)

Aspect ratio: 3.2

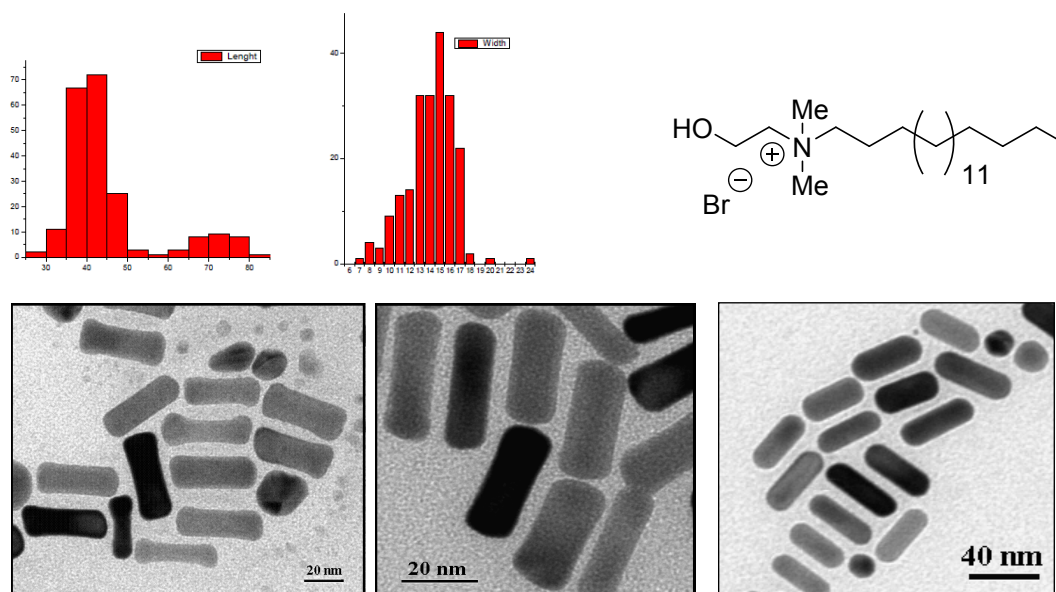


Figure ESI3. TEM images and size distributions of AuNP @ HEA18Br

2.4 Gold Nanoparticles obtained with HEA12Br

Pictures obtained from samples prepared with 24 hours.

Mean size: 18,8 nm x 8,0 nm ($\pm 3,4$ nm x 0,6 nm)

Aspect ratio: 2.3

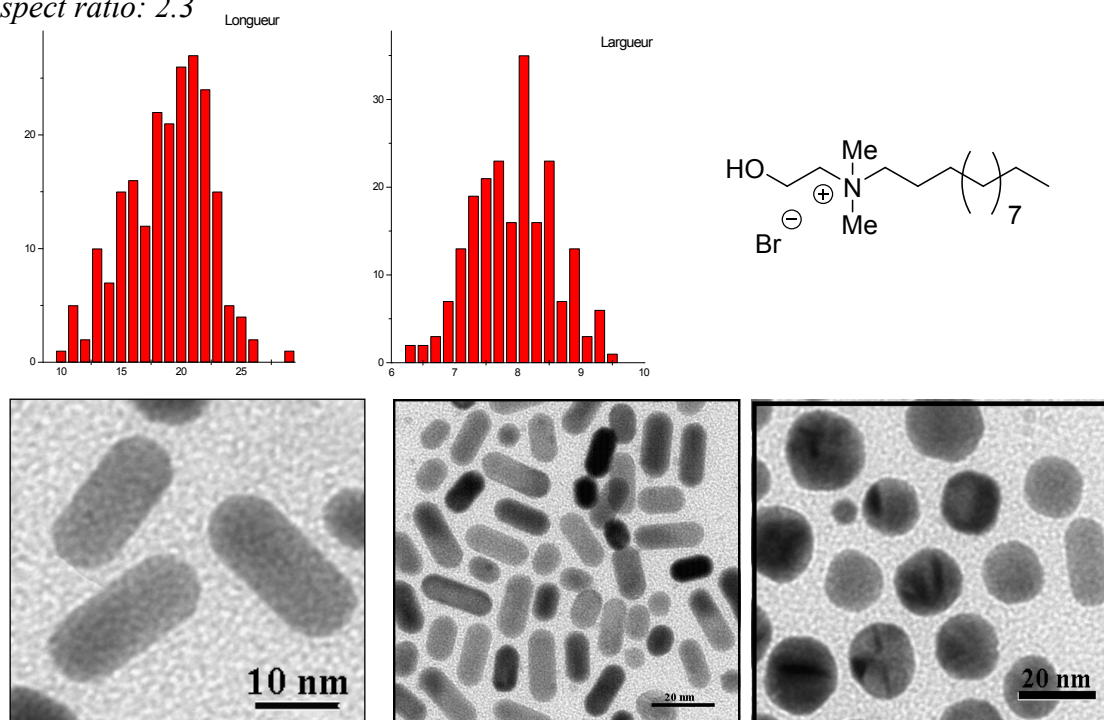


Figure ESI4. TEM images and size distributions of AuNP @ HEA12Br

2.5 Gold Nanoparticles obtained with HEA16Cl

Pictures obtained from samples prepared with 24 hours.

Mean size: 10 nm ($\pm 1,7$ nm)

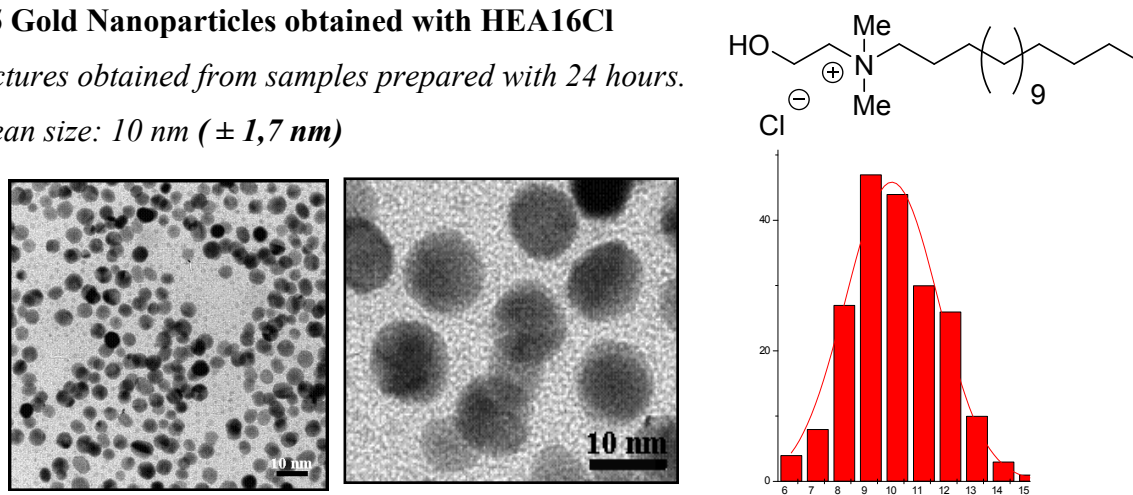


Figure ESI5. TEM and size distribution of AuNP @ HEA16Cl

2.6 Gold Nanoparticles obtained with HEA16F

Pictures obtained from samples prepared with 24 hours.

Mean size: 8,5 nm ($\pm 1,0$ nm)

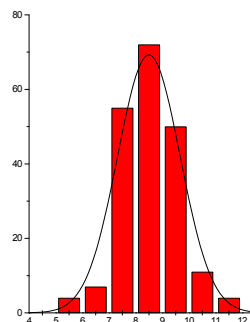
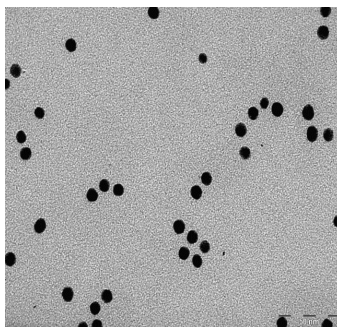
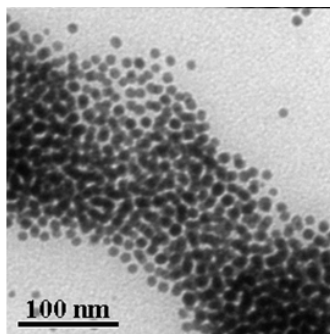
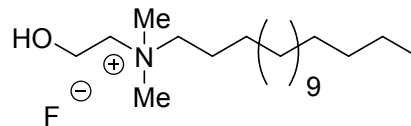


Figure ESI6. TEM and size distribution of AuNP @ HEA16F

2.7 Gold Nanoparticles obtained with HEA16I

Pictures obtained from samples prepared with 24 hours.

Mean size: 80 nm

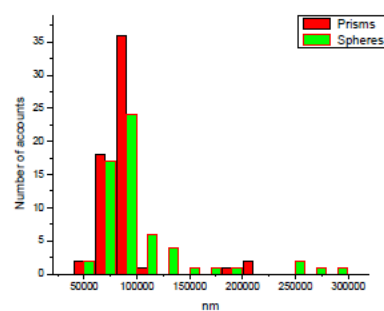
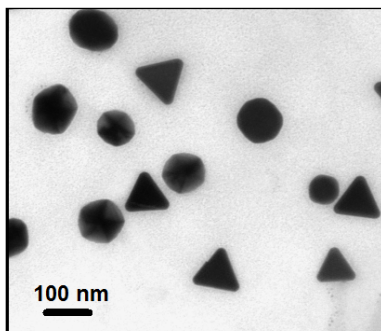
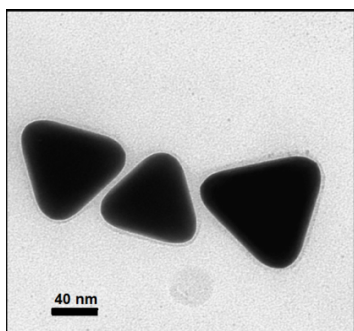
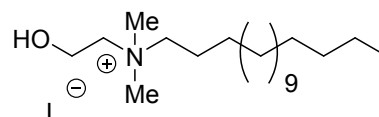


Figure ESI7. TEM images of AuNP @ HEA16I

2.8 Gold Nanoparticles obtained with HEA16HCO3

Pictures obtained from samples prepared with 24 hours.

Mean size: 29 nm x 7 nm ($\pm 6,0$ nm x 2.3 nm)

Aspect ratio: 4.14

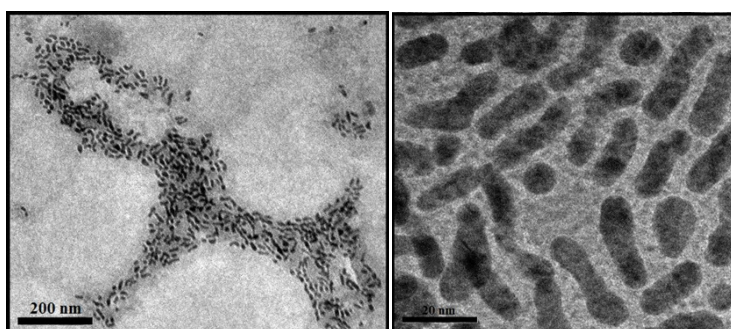
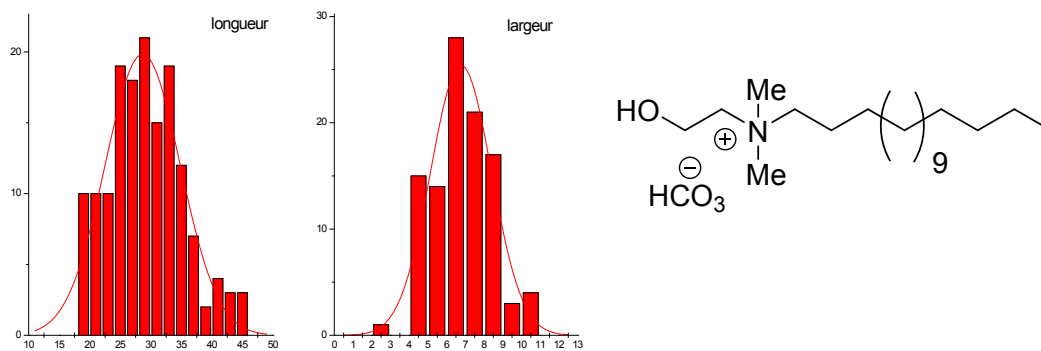


Figure S18. TEM and size distributions of AuNP @ HEA16HCO3